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A Review: Analysis Atomic Absorption Spectrometry (AAS) of Heavy Metal Content in Crude Palm Oil

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ABSTRACT

Indonesia, the world's largest producer of crude palm oil (CPO), turns its oil through a series of refinement processes that include degumming, bleaching, and deodorization before it is used as cooking oil. Still, heavy metals are the main focus of CPO research. Elements known as heavy metals can have harmful effects on the human body, even in small doses. Making sure the amount of metal in CPO doesn't go over the limit is crucial. To find out how much this ingredient contributes to the heavy metal contamination in crude palm oil, more research is required. The CPO refining process is carried out with the aim of reducing free fatty acids and removing dirt or metals dissolved in CPO, which can affect the quality of cooking oil. AAS can detect metals in small amounts and provide analytical differences of up to 0.006 mg/kg.

1. Introduction

The palm oil industry has been an important economic contributor for countries like Indonesia Malaysia, Thailand, and other tropical developing regions. Palm oil is a commodity that Indonesia can export well because it is the world's largest producer of palm oil [1]. According to Rosita (2014), Indonesia provides 47% of the world's palm oil needs [2], palm oil is composed of the following components: 0.03% carotene, 0.07% aldehyde, 0.2% water [3], 4.57% free fatty acids, and 95% triglycerides [4]. Palm oil processing not only produces palm oil, but also produces waste. Even though nearly all literature on palm oil or palm oil mill effluent (POME) treatment reports impressive export and production figures, it is not surprising that the effluent's massive production has turned out to be a major source of water pollution [5]. Liquid waste from palm oil needs to be the center of attention, about 60% of all waste produced in palm oil mills comes from the processing of fresh fruit bunches Industrial liquid waste typically includes heavy metals [6]. Heavy metals are elements that have a density of more than 4 gr/cm3 [7-8].

Wastewater with an industrial basis can produce heavy metals that can include a wide variety of elements. These components fall into hazardous heavy metals, such as arsenic (As), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), chromium (Cr), and nickel (Ni) [9]. The contaminated wastewater contains metal elements, of which are invisible to the unaided eye. But it's frequently the underlying cause of a number of serious health problems. When heavy metal levels are low, they can have harmful effects that obstruct enzyme function and cause metabolic disruptions in the body. Heavy metals can therefore be allergens, carcinogens, or mutagens for both people and animals [10]. Thus, researchers now face a significant challenge in removing toxic heavy metals from the environment on a large scale. In low doses, heavy metals can cause toxic effects that block the work of enzymes, disrupting the body's metabolism. As a result, heavy metals can cause allergies, carcinogens, or mutagens in humans and animals [10]. CPO cooking oil products contain heavy metals, which are pollutants and are difficult to break down. These metals will also affect the stability of the oil produced [11]. The heavy metal content is biodegradable and, at certain levels, can be toxic to the body, so heavy metals in cooking oil must meet quality standards [12]. It is very important to ensure that the heavy metal content in cooking oil does not exceed the threshold. In his research.

Hasibuan (2011) reported that the metal content continues to increase in proportion to the number of frying repetitions and the impact of heavy metal pollution in the frying equipment. Further studies are needed to find out how much this component contributes to heavy metal pollution in crude palm oil [13]. The CPO refining process is carried out with the aim of reducing free fatty acids and removing impurities or metals dissolved in CPO, which can affect the quality of cooking oil [14] [13]. This discussion focuses on analysing heavy metal content using several methods that can measure heavy metal levels in excessive amounts. The CPO refining process based on research that has been carried out is highlighted in this review. This review article aims to learn about the Atomic Absorption Spectrometry (AAS) method used to determine the content of heavy metals in a product.

2. Crude Palm Oil Refining Process

The refining process is carried out to change raw materials into products of greater value. In the cooking oil processing process, the process of refining palm oil will produce a product that has a brighter color, has no taste, and has stability. The refining process aims to remove components that have disturbing properties in oil products and also minimize damage [15]. The CPO refining process, namely degumming, bleaching, and deodorization, is carried out to remove several components during the refining process, such as free fatty acids (FFA), aldehydes, ketones, and several volatile components [16] and remove the odor by removing impurities. contained in crude palm oil (CPO) [3]. Degumming is carried out to minimize gums (phospholipids, proteins, residues, and carbohydrates) in the oil without reducing the amount of free fatty acids in the oil [17], [18]. This process is carried out by separating phosphatide compounds from the water phase, which can be separated by precipitation, filtration, or centrifugation [19]. There are many ways to carry out degumming, such as using sodium chloride [20], H2SO4 [21], and enzyme [22].

Accorrding Irwan (2013), the air and acid degumming process was also effective for separating sap and gum in oil because acid can bind impurities in oil, such as metals, in the form of phosphatides [16]. According to research conducted by Ali (2012), phosphorus levels in CPO fell to 42.1 ppm before degumming and 33.1 ppm after degumming. After degumming, palm oil (CPO) is bleached using activated charcoal at a temperature of 120 °C [23]. Bleaching earth is used in the bleaching process to lighten the color, reduce metal levels, adsorb phospholipids, and remove phosphoric acid in oil after degumming [24]. Meanwhile, the deodorization process is carried out at high temperatures to remove free fatty acids and odors, and if the type of bleaching earth used is not suitable and its adsorption capacity is low, then the refined product still contains metals in certain concentrations [25]. The results of the analysis of heavy metal levels in crude palm oil before and after prevention are presented in Table 1 [13].

Tabel 1. CPO heavy metal content before and after refining

Heavy Metals	Before refining (ppm)	Decline rate %	
		Bleaching	Deodorization
P	13.218	87.7	95.3
Fe	4.058	97.3	99.1
Cu	0.053	26.8	37.8

From Table 1, it is shown that after the bleaching process, a significant reduction rate occurred in P and Fe. The heavy metals contained in palm oil are difficult to reduce and remove. According to this research, metals remain contained in small amounts in the oil during the refining process. However, the refining process is very helpful in reducing the amount of metal to the set standards [13].

3. Heavy Metals in Crude Palm Oil

Any species of metal (or metalloid) that appears in an unwelcome location or at a concentration or form that has a negative impact on people or the environment could be classified as a "contaminant". Heavy metals may accumulate in the body as a result of ongoing exposure, which could be harmful [26]. Although humans require certain heavy metals, such as iron, zinc, copper, chromium, cobalt, and manganese [27], [28], their presence at high concentrations above maximum permissible limits. Heavy metals can contaminate the crude palm oil refining process. The level of heavy metals in palm oil depends on the impurities found in the machine during the extraction process. Final products containing metals undergo oxidative reactions that change their color, taste, and dor. Metal ions, especially iron and copper, react with hydrogen peroxide, causing oxidation reactions and oil damage[29] [14]. The negative effects of heavy metals are not necessarily caused only by non-essential metals. Essential metals can also be detrimental in terms of both toxicity and deficiency. Metals that are essential metals that the body needs in small amounts are Zn, Cu, Fe, Mn, Co, and Se. Excessive amounts of this metal are toxic to the body. Metal toxicity has several adverse effects on humans, the most important being tissue damage, especially detoxification and the development of excreted tissues (liver and kidney). Some metals have carcinogenic (carcinogenic) and teratogenic (organ teratogenic) properties. [30].

Tabel 2. Contamination heavy metals in CPO

Parameters	Condition (mg/kg)
Cadmium (Cd)	0.5
Lead (Pb)	0.1
Nickel Ni	0.2
Mercury (Hg)	0.05
Arsenic (As)	0.1

Table 2 shows the maximum permitted levels of heavy metals in cooking oil according to the research [31]. To examine the level of danger or not of heavy metals in crude palm oil, a heavy metal content measuring instrument is needed. The following section will discuss instruments that can be used to measure heavy metal content.

4. Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) is a quantitative metal analysis technique that can be used to identify around seventy elements. This method measures the concentration of an element by passing light of a certain wavelength emitted by a radiation source containing a certain element through a cloud of sample atoms. Hollow cathode lamps (HCL) are an energy source that will absorb light from atoms [32]. Hasibuan (2011) conducted research to standardize crude palm oil (CPO) using atomic absorption spectrometry. The Cu content of pure crude palm oil is 0.053 mg/kg, but after the bleaching and deodorization processes, the Cu content decreases to 0.038 mg/kg and 0.032 mg/kg [13]. Atomic Absorption Spectrometry (AAS) can detect metals in small amounts and provide analytical differences of up to 0.006 mg/kg, according to research results [33]. Table 3. provides a summary of the maximum acceptable limit for heavy metals found in food products using the Atomic Absorption Spectrometry AAS method.

Table 3. Maximum limit for heavy metals using AAS method

Heavy metal	Maximum limits (mg/kg)	References
Cadmium (Cd)	0.3	[34-35]
Lead (Pb)	1.0	[10]
Cobalt (Co)	0.043	[36]
Arsenic (As)	1.4	[29]
Mercury (Hg)	0.5	[35-36]
Nickel (Ni)	0.10	[35-36]
Chromium	0.10	[34]

Research conducted by Maurya (2021) which analyzed metal content using AAS was also successfully carried out. The permissible limit of heavy metal in the soil (mg/kg) is Cd (6), Zn (600), Mn (20), Pb (500), Cu (270), Ni (75), Cr (50) [18]. Quantification of heavy metals eight heavy metals, including cadmium (Cd), lead (Pb), cobalt (Co), manganese (Mn), mercury (Hg), arsenic (As), chromium (Cr), and nickel (Ni), were found in all samples analyzed using the AAS method.

5. Conclusion

Based on studies that have been carried out, the crude palm oil refining process can reduce FFA levels in CPO to remove gum or sap and reduce the amount of metals to the specified standards. Atomic Absorption Spectrometry (AAS) can analyze small amounts of metal content

References

[1] P. Setyopratomo, "Produksi Asam Lemak dari Minyak Kelapa Sawit Dengan Proses Hidrolisis," J. Tek. Kim., vol. 7, no. 1, pp. 26–31, 2012.

[2] R. Rosita, Haryadi, and Amri, "Determinan Ekspor CPO Indonesia Ratih Rosita, Haryadi, Amril Program Magister Ilmu Ekonomi Fakultas Ekonomi dan Bisnis Universitas Jambi," J. Perspekt. Pembiayaan dan Pembang. Drh., vol. 1, no. 4, pp. 183–190, 2014.

[3] L. Ifa, L. Wiyani, N. Nurdjannah, A. M. T. Ghalib, S. Ramadhaniar, and H. S. Kusuma, "Analysis of bentonite performance on the quality of refined crude palm oil's color, free fatty acid and carotene: the effect of bentonite concentration and contact time," Heliyon, vol. 7, no. 6, p. e07230, 2021, doi: 10.1016/j.heliyon.2021.e07230.

[4] D. O. Putri, E. Mardawati, S. H. Putri, and D. Frank, "Perbandingan Metode Degumming CPO (Crude Palm Oil) terhadap Karakteristik Lesitin yang Dihasilkan," J. Ind. Pertan., vol. 1, no. 3, pp. 88–94, 2019, [Online]. Available: http://jurnal.unpad.ac.id/justin

[5] W. L. Liew, M. A. Kassim, K. Muda, S. K. Loh, and A. C. Affam, "Conventional methods and emerging wastewater polishing technologies for palm oil mill effluent treatment: A review," J. Environ. Manage., vol. 149, pp. 222–235, 2015, doi: 10.1016/j.jenvman.2014.10.016.

[6] J. Wulandari, S. Pengajar Jurusan Fisika, and F. Universitas Negeri Padang, "Analisis Kadar Logam Berat pada Limbah Industri Kelapa Sawit Berdasarkan Hasil Pengukuran Atomic Absorption Spectrophotometry (AAS) Mahasiswa Fisika, FMIPA Universitas Negeri Padang 2)," Pillar Phys., vol. 8, pp. 57–64, 2016.

[7] N. Abdullah, N. Yusof, W. J. Lau, J. Jaafar, and A. F. Ismail, "Recent trends of heavy metal removal from water/wastewater by membrane technologies," J. Ind. Eng. Chem., vol. 76, pp. 17–38, 2019, doi: https://doi.org/10.1016/j.jiec.2019.03.029.

[8] A. Aprile and L. De Bellis, "Editorial for special issue 'heavy metals accumulation, toxicity, and detoxification in plants,'" Int. J. Mol. Sci., vol. 21, no. 11, pp. 1–5, 2020, doi: 10.3390/ijms21114103.

[9] W. Altowayti, H. Almoalemi, S. Shahir, and N. Othman, “Comparison of culture-independent and dependent approaches for identification of native arsenic-resistant bacteria and their potential use for arsenic bioremediation,” Ecotoxicol. Environ. Saf., vol. 205, p. 111267, Dec. 2020, doi: 10.1016/j.ecoenv.2020.111267.

[10] A. Aminah, R. Rahmawati, T. Naid, and S. Salma, “Analisis Kadar Arsen (As) dan Timbal (Pb) Pada Minyak Goreng Pemakaian Berulang dengan Metode Spektrofotometri Serapan Atom,” J. Ilm. As-Syifaa, vol. 9, no. 1, pp. 11–16, 2017, doi: 10.33096/jifa.v9i1.235.

[11] H. A. Hasibuan, “Study on Characteristics of Indonesian Palm Kernel Oil and Its Fractionation Products,” J. Standarisasi, vol. 14, no. 2, pp. 98–104, 2018, [Online]. Available: https://scholar.google.com/scholar

[12] M. Musthofa and L. S Fikri, “Pupuk Cair Organik dari Limbah Bioetanol dan Limbah Ternak Kambing: Analisis Kadar N, P, dan K,” J. Sos. Sains, vol. 2, no. 1, pp. 210–218, 2022, doi: 10.59188/jurnalsosains.v2i1.360.

[13] hasrul abdi Hasibuan and E. Nuryanto, “Kajian Kandungan P, Fe, Cu, dan Ni Pada Minyak Sawit, Minyak Inti Sawit Dan Minyak Kelapa Selama Proses Rafinasi,” J. Stand., vol. 13, no. 1, pp. 61–66, 2011, [Online]. Available: https://js.bsn.go.id/index.php/standardisasi/article/view/23

[14] Y. Afrizal et al., “Pengolahan Crude Palm Oil (Cpo) Menjadi Minyak Sawit Merah (Msm) Menggunakan Filter Batuan Zeolit, Membran Keramik Dan Cartridge Filter Processing of Crude Palm Oil (Cpo) Into Red Palm Oil(Rpo) Using Zeolite, Ceramic Membrane and Cartridge Filter,” J. Kinet., vol. 13, no. 03, pp. 11–19, 2022, [Online]. Available: https://jurnal.polsri.ac.id/index.php/kimia/index

[15] Soni Fajar Mahmud, “Proses Pengolahan CPO (Crude Palm Oil) menjadi RBDPO(Refined Bleached and Deodorized Palm Oil) di PT XYZ Dumai,” J. Unitek, vol. 12, no. 1, pp. 55–64, 2019, doi: 10.52072/unitek.v12i1.162.

[16] C. Irawan, A. Tiara, Nur, and H. Sherly, Uthami, w, p, “Pengurangan Kadar Asam Lemak Bebas (Free Fatty Acid) dan Warna dari Minyak Goreng Bekas Dengan Proses Adsorpsi Menggunakan Campuran,” Progr. Stud. Tek. Kim. Fak. Tek. Univ. Lambung Mangkurat, vol. 2, no. 2, pp. 29–33, 2013.

[17] L. M. Serrano-Bermúdez et al., “Kinetic models for degumming and bleaching of phospholipids from crude palm oil using citric acid and Super Flo B80® and Tonsil®,” Food Bioprod. Process., vol. 129, pp. 75–83, 2021, doi: 10.1016/j.fbp.2021.07.005.

[18] K. A. Sampaio et al., “Impact of Crude Oil Quality on the Refining Conditions and Composition of Nutraceuticals in Refined Palm Oil,” J. Food Sci., vol. 82, no. 8, pp. 1842–1850, 2017, doi: 10.1111/1750-3841.13805.

[19] W. Irawan and A. Amri, “Penentuan Kadar Bleaching Earth dan Phosporic Acid pada Proses Degumming dan Bleaching Crude Palm Oil,” J. Bioprocess, Chem. Environ. Eng. Sci., vol. 2, pp. 1–14, 2021.

[20] R. Hernando, “Perbaikan Kualitas Minyak Biji Karet melalui Proses Degumming Menggunakan Zeolit dan Karbon Aktif sebagai Bahan Baku Pembuatan Biodiesel,” J. Tek. Mesin, vol. 02, no. 01, pp. 73–80, 2013.

[21] A. M. Qiqmana and D. H. Sutjahjo, “Karakteristik Biodiesel Dari Minyak Biji Nyamplung Denganproses Degumming Menggunakanasam Sulfat Dan Asam Cuka,” J. Tek. Mesin Unesa, vol. 2, no. 2, pp. 132–139, 2014.

[22] A. Nur, A. Hamid, Y. Ismi, and H. Indah “Biodegumming Rami Menggunakan Enzim Amobil dari Cairan Rumen Sapi ” Jurnal Teknik Kimia. 96–100, 2013.

[23] M. Ali, " Pemucatan Minyak Sawit Mentah Menggunakan Arang Aktif," Jurnal Teknik Kimia vol. 6, no. 2, pp. 41–45, 2012.

[24] T. Hasballah and L. H. Siregar, "Analisa Pemakaian Jumlah BE (Bleaching Earth) Terhadap Kualitas Warna DBPO (Degummed Bleached Palm Oil) Pada Tangki Bleacher (D202) dengan Kapasitas 2000 Ton / Hari di Unit Refinery PT. Smart Tbk Belawan," J. Teknol. Mesin UDA, vol. 1, no. 1, pp. 9–16, 2020.

[25] S. Sutanto and A. Abriana, "Penerapan Teknologi Pemurnian Minyak Goreng Rakyat Pada Masyarakat Pengolah Minyak Goreng," *J. Din. Pengabdi.*, vol. 1, no. 2, pp. 153–160, 2016.

[26] M. Bonić *et al.*, "The contents of heavy metals in Serbian old plum brandies," *J. Serbian Chem. Soc.*, vol. 78, no. 7, pp. 933–945, 2013, doi: 10.2298/JSC121106016B.

[27] E. Baranyai, E. Simon, M. Braun, B. Tóthmérész, J. Posta, and I. Fábián, "The effect of a fireworks event on the amount and elemental concentration of deposited dust collected in the city of Debrecen, Hungary," *Air Qual. Atmos. Heal.*, vol. 8, no. 4, pp. 359–365, 2015, doi: 10.1007/s11869-014-0290-7.

[28] P. Olmedo, A. F. Hernández, A. Pla, P. Femia, A. Navas-Acien, and F. Gil, "Determination of Essential Elements (Copper, Manganese, Selenium And Zinc) in Fish and Shellfish Samples. Risk and Nutritional Assessment And Mercury–Selenium Balance," Food Chem. Toxicol., vol. 62, pp. 299–307, 2013, doi: https://doi.org/10.1016/j.fct.2013.08.076.

[29] T. Agustina and F. Teknik, "Kontaminasi Logam Berat Pada Makanan Dan Dampaknya Pada Kesehatan," *Teknobuga*, vol. 1, no. 1, pp. 53–65, 2014.

[30] S. Taurusiana, N. Afiati, and N. Widyorini, "Kajian Kandungan Logam Berat Besi (Fe) dan Seng (Zn) pada Jaringan Lunak Kerang Darah (Anadara Granosa (L.)) Di Perairan Tanjung Mas, Semarang Dan Perairan Wedung, Demak," *Manag. Aquat. Resour. J.*, vol. 3, no. 1, pp. 143–150, 2014, doi: 10.14710/marj.v3i1.4431.

[31] V. C. Isiodu, B. M. Onyegeme-okerenta, and E. B. Essien, "Dietary Exposure and Risk Characterization of Selected Toxic Metals in Crude Palm Oil (Elaeis guineensis Jacq) from six states in Niger Delta , Nigeria," vol. 10, no. 01, pp. 25–37, 2024.

[32] F. Abrham and A. V Gholap, "Analysis of Heavy Metal Concentration in Some Vegetables Using Atomic Absorption Spectroscopy," *Pollution*, vol. 7, no. 1, pp. 205–216, 2021, doi: 10.22059/poll.2020.308766.877.

[33] N. Andarwulan *et al.*, "Stabilitas Fotooksidasi Minyak Goreng Sawit Yang Difortifikasi Dengan Minyak Sawit Merah," *J. Teknol. dan Ind. Pangan*, vol. 27, no. 1, pp. 31–39, 2016, doi: 10.6066/jtip.2016.27.1.31.

[34] F. Additives, "Evaluation of certain food contaminants," World Health Organization Technical Report Series," vol. 930. 2006.

[35] C. A. Commission, "Report of the 33rd session of the Codex Committee on Food Additives and Contaminants. Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, The Hague, The Netherlands," no. March, pp. 2–7, 2001.

[36]K. O. Omeje *et al.*, "Absorption Spectroscopy (AAS) and Gas Chromatography (GC)," Toxins-Mdpi, vol. 13, no. 870, pp. 1–17, 2021, [Online]. Available: https://doi.org/10.3390/toxins13120870%0AReceived