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Halal enzymatic cosmetic ingredients: The role of enzymes in ingredients selection

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ABSTRACT

The rising demand for halal products, especially within the cosmetics industry, has increased the need for cosmetic products to comply with Islamic laws. One of the challenges in achieving halal certification is the determination of the source of the active ingredients used in cosmetic products, such as enzymes. According to Islamic laws, enzymes derived from pigs or other animals that are not slaughtered are not considered halal. To ensure that the enzymes used in cosmetics are derived from halal sources, it is necessary to use enzymes generated from microorganisms through fermentation, provided that the raw materials and growth medium comply with Islamic laws. Additionally, halal cosmetics must meet regional and international standards, including the Indonesian Ulema Council's Fatwa and the Malaysian Cosmetic and Personal Care Standards. This research provides a comprehensive review of the role of enzymes in selecting halal compliance cosmetic ingredients, focusing on the source of enzymes as a means of assessing the halalness of cosmetic products. It is essential to utilize halal enzymes such as those derived from plants to provide Muslim consumers with assurance when using cosmetic products.

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1 Introduction

Cosmetic products can be defined as any substances that can be applied on the external surface of the human body such as the hair, skin, lips, and other part of the body for protecting, beautifying, cleansing, and preventing body odor or protecting the body from infection and microorganisms (Fatima *et al.* 2020). These products also represent a symbol of beauty for women. Indonesia, with a female population of 133.54 million in 2020, is a promising market environment for the cosmetic industry (Aufi & Aji 2021; Cabinet Secretariat of The Republic of Indonesia 2021).

The global Muslim population is estimated to be 1.8 billion individuals, representing 24% of the global population. The Muslim population is projected to grow at double the rate of the global population during the next few decades. In 2010, Indonesia, Pakistan, and India were the three nations with the highest Muslim populations. Indonesia leads globally with approximately 231 million Muslims, constituting 93% of its adult population. Islam dominates in Indonesia, with over 87% of the population identifying as Muslim (Hackett *et al.* 2015).

According to The Business Research Company (2023), the worldwide halal cosmetics market size in 2022 is about $32.50 billion, and it is predicted to expand at a pace of 13.8% in 2027, with a market size of $62.65 billion by 2027. Globally, the halal market is predicted to grow every single year. According to a report by Dinar Standard (2020), the state of the Global Islamic Economy Report 2020, global Muslim expenditure on cosmetics increased by 3.4% from 2018 to 2019, is approximately $66 billion. Following the emergence of COVID-19, it is forecasted that Muslim consumer spending on cosmetics will decline by 2.5% in 2020. A projected 5-year Compound Annual Growth Rate (CAGR) of 2.9% is expected despite the temporary setback, leading to a forecasted total of $76 billion in Muslim spending on cosmetics by the year 2024 (Fahmi 2017).

The growing Muslim population is expected to drive the expansion of halal cosmetics businesses in the upcoming years. The phrase "growth in Muslim population" refers to an increase in the number of Muslims in a certain region, country, or planet, which may occur due to some reasons, such as increased birth rates within Muslim households. Muslim immigration and conversion to Islam may also contribute to this growth. As the Muslim population increases, the demand for halal cosmetics that align with their religious beliefs rises. According to the Pew Research Center, the global Muslim population is expected to reach 2.2 billion by 2030. Consequently, this growing Muslim population will drive the future expansion of the halal cosmetics industry (Hackett *et al.* 2015).

According to Islamic laws, some ingredients are prohibited in halal cosmetic products, such as those derived from pigs, carrions, blood, human body parts, predatory animals, reptiles, and insects. To attain halal certification, cosmetic materials obtained from permissible animals must be slaughtered in accordance with Islamic law. The foundation of halal cosmetics involves the selection and processing of ingredients, ensuring they comply with Islamic dietary regulations. Enzymatic methods play a crucial role in this process, facilitating the extraction, modification, and certification of components to ensure halal compliance throughout manufacturing. The global enzymes market is projected to grow by 14% annually, reaching $15.25 billion by 2025 (The Business Research Company 2021).

Halal cosmetic products must exclude forbidden ingredients such as pigs, carrion, blood, human body parts, predatory animals, reptiles, and insects. Moreover, ingredients derived from permissible animals must be sourced from those slaughtered according to Islamic law to be considered halal. At the core of halal cosmetics is the intricate process of selecting and processing ingredients, focusing on sourcing, modifying, and certifying components in accordance with Islamic dietary laws. Enzymatic techniques are crucial in this effort, enabling the extraction, modification, and certification of ingredients to ensure halal compliance throughout production. The global enzymes market is projected to grow by 14% annually, reaching $15.25 billion by 2025 (The Business Research Company 2021). Therefore, thjs research aims to provide a comprehensive examination of the role of enzymes in the selection of halal compliance cosmetic ingredients.

2 Halal, Haram, and Najs Principle

In Islam, the Halal concept is based on Shariah Law, obtained from the Qur'an, sunnah, the consensus of Islamic jurists (ijma'), analogy (qiyas), and the method of legal reasoning (ijtihad). Halal denotes actions or items that are permissible and unprohibited under Islamic law. This stands in contrast to haram, which signifies actions or items considered impermissible

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in Islam. A reward is given to those who follow halal law, but sin is for those who do not believe. (Kashim *et al.* 2023). Several verses in the Qur'an mention halal and haram terms. The 2 are Surah al-Baqarah verse 168 and Surah al-Maidah verse 3 described below.

اَيُّهَا النَّاسُ كُلُوْا مِمَّا فِى الْاَرْضِ حَلٰلًا طَيِّبًا وَّلَا تَتَّبِعُوْا خُطُوٰتِ الشَّيْطٰنِ اِنَّه
لَكُمْ عَدُوٌّ مُّبِيْنٌ

"O mankind, eat from whatever is on earth [that is] lawful and good and do not follow the footsteps of satan. Indeed, he is to you a clear enemy." (QS. al-Baqarah [2]: 168).

حُرِّمَتْ عَلَيْكُمُ الْمَيْتَةُ وَالدَّمُ وَلَحْمُ الْخِنْزِيْرِ وَمَآ اُهِلَّ لِغَيْرِ اللّٰهِ بِه وَالْمُنْخَنِقَةُ
وَالْمَوْقُوْذَةُ وَالْمُتَرَدِّيَةُ وَالنَّطِيْحَةُ وَمَآ اَكَلَ السَّبُعُ اِلَّا مَا ذَكَّيْتُمْۗ وَمَا ذُبِحَ عَلَى
النُّصُبِ وَاَنْ تَسْتَقْسِمُوْا بِالْاَزْلَامِ ذٰلِكُمْ فِسْقٌ اَلْيَوْمَ يَىِٕسَ الَّذِيْنَ كَفَرُوْا مِنْ دِيْنِكُمْ
فَلَا تَخْشَوْهُمْ وَاخْشَوْنِ اَلْيَوْمَ اَكْمَلْتُ لَكُمْ دِيْنَكُمْ وَاَتْمَمْتُ عَلَيْكُمْ نِعْمَتِيْ
وَرَضِيْتُ لَكُمُ الْاِسْلَامَ دِيْنًا فَمَنِ اضْطُرَّ فِيْ مَخْمَصَةٍ غَيْرَمُتَجَانِفٍ لِّاِثْمٍ فَاِنَّ اللّٰهَ
غَفُوْرٌ رَّحِيْمٌ

"Prohibited to you are dead animals, blood, the flesh of swine, and that which has been dedicated to other than Allah, and [those animals] killed by strangling or by a violent blow or by a head-long fall or by the goring of horns, and those from which a wild animal has eaten, except what you [are able to] slaughter [before its death], and those which are sacrificed on stone altars, and [prohibited is] that you seek decision through divining arrows. That is grave disobedience. This day those who disbelieve have despaired of [defeating] your religion; so fear them not, but fear Me. This day I have perfected for you your religion and completed My favor upon you and have approved for you Islam as religion. But whoever is forced by severe hunger with no inclination to sin – then indeed, Allah is Forgiving and Merciful." (QS. Al-Ma'idah [5]: 3).

Meanwhile, according to MS1500:2019, Shariah law and fatwa describe najs as impurities. These laws include a) dogs, pigs, and their progeny, b) Halal food tainted with non-halal substances, c) Halal food directly exposed to non-halal elements, d) any fluids and objects extracted from human or animal orifices, such as urine, blood, vomit, pus, feces, and placenta, e) carcasses or halal animals not slaughtered in accordance with Shariah law and fatwa, excluding aquatic animals and certain insects, and f) Khamr (intoxicating liquor) and edible or beverages containing or mixed with khamr, prohibited by Shariah law and fatwa (Malaysian Standard 2019a).

According to the Indonesian Ulema Council's Fatwa (2013), there should be lawful use of cosmetics for decorative purposes, which includes a) the materials used are halal and pure, b) intended for interests that are permissible according to sharia, and c) the materials that will be used in the production process should not be dangerous. Cosmetic products containing ingredients produced through genetic engineering involving pig or human genes are considered harmful. Furthermore, cosmetic products manufactured using ingredients such as raw materials, active ingredients, and/or additional ingredients from halal animal derivatives (such as fat) with an unknown method of slaughter are considered makruh tahrim and should be avoided. Similarly, cosmetic products manufactured using ingredients from microbial products where the origin of the microbial growth medium is uncertain (particularly if it's from pigs) should be avoided until there is clarity regarding the halalness and purity of the ingredients (Majelis Ulama Indonesia 2013).

3 Enzyme

Enzymes are biological catalysts, also known as biocatalysts that accelerate the metabolic processes in living organisms. Additionally, these catalysts can be isolated from cells and applied to catalyze a variety of commercially significant processes. Enzymes are classified according to the process they catalyze, and categorized based on the EC (Enzyme Commission) number. The term "enzyme" can refer to a single enzyme protein or a collection of proteins sharing a common catalytic characteristic. Completely distinct protein folds are known to catalyze the same reaction and consequently have the same EC value. These enzymes are called nonhomologous iso-functional enzymes (NISE) (Omelchenko *et al.* 2010). The oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases were characterized as six enzyme classes or EC levels. Translocases were categorized into a seventh enzyme category (EC 7) that was added to the EC in August 2018. The key factors in enzyme categorization are evolutionary and biophysical models, which allow the development of structural similarity and sequence knowledge (Vandenberghe *et al.* 2020).

Similar to other catalysts, enzymes have two fundamental properties. First, they increase the rate of chemical reactions without being consumed or permanently altered. Second, they increase the reaction rate without changing the chemical equilibrium between reactants and products. To bind a substrate to an enzymes active site, the lock and key model and the induced fit model are applied. The first concept shows that the structure and chemistry of the substrate are complementary to the shape and chemistry of the enzymes active site. This implies that when the substrate approaches the active site, it fits exactly and bonds with the enzymes, producing an enzymes-substrate complex. The second proposes that the enzymes and substrate do not have the exact complementary shape/chemistry or alignment from the start. However, this alignment was generated at the active site by substrate binding. Local molecular interactions with amino acid residues on the polypeptide chain often stabilize substrate binding to enzymes (Lewis & Stone 2023).

4 Enzyme used in cosmetics ingredients

In the cosmetic industry, enzymes are often used in the compositions to help reduce acne, skin aging, and pigmentation. Other functions include exfoliation of the skin, preventing the formation of free radicals that can harm the skin and body, maintaining firm skin, and antibacterial effects. Cosmetic enzymes can significantly impact the skin microbiome, a vital collection of microorganisms for skin barrier function and homeostasis. These microbiomes produce protease enzymes essential for desquamation and renewal of the stratum corneum. Additionally, pH levels are regulated by sebum and free fatty acid synthesis, while lipase enzymes aid in breaking down the lipidic film on the skin's surface. These processes are crucial for overall skin health and function. Enzymes in cosmetics can affect the skin's microbiome in several ways: they can alter the skin's pH, influencing microorganism development and survival; disturb the skin's natural barrier, increasing susceptibility to infections and disorders; and enhance the proliferation of beneficial microorganisms. Some cosmetic enzymes, such as proteolytic, may stimulate the growth of healthy bacteria on the skin (Boxberger *et al.* 2021).

It is important to ensure that enzymes used in cosmetics come from halal sources and that this is clearly stated on the product label. Although there is no specific information available on halal microbial enzymes used in cosmetics. Enzymes generated from microorganisms during fermentation, on the other hand, are halal if the raw materials or other substances used in the growing medium are halal (Grocholl 2023).

A product's enzymes derived from non-halal sources or made with non-halal or questionable ingredients cannot be considered halal even though it has the label (Fischer 2015). To achieve halal accreditation, it is important to analyze the origins and manufacturing methods of enzymes used in the cosmetic industry. Haram enzymes are either obtained from haram animals or manufactured with haram ingredients. Enzymes produced by microorganisms during fermentation are considered halal if neither the development medium nor the final product contains any haram components. Enzyme-producing genetically modified microorganisms are not permitted to use recombinant DNA derived from haram or questionable sources (Ermis 2017). Examples of regional and international standards of halal cosmetics are the Indonesian Ulema Council Fatwa Number 26 of 2013 and The Malaysian Cosmetic and Personal Care Standard (MS2200:PART1:2008) (Majelis Ulama Indonesia 2013; Malaysian Standard 2019b).

Enzymocosmetics is a term used in the cosmetics industry to describe cosmetic products manufactured using proteolytic enzymes that specifically hydrolyze the peptide bonds of proteins within the stratum corneum, which are widely recognized for their ability to enhance skin health and appearance (Gomes & Damazio 2013; Kočevar Glavač *et al.* 2015). These products promote biological exfoliation, and faster skin regeneration, provide deep cleansing, and improve the penetration of cosmetically active substances (Monteiro & Silva 2009). The stratum corneum becomes thinner, resulting in increased skin flexibility and texture. Some primary plant enzymes are used for skin exfoliation, which includes papain from papaya, bromelain from pineapple, and ficain from fig trees (Gonçalves 2021).

Papain (EC 3.4.22.2) is an endopeptidase-like proteolytic enzyme present in papaya fruits (Carica papaya) at a concentration of approximately 8%. This enzyme contains a thiol group that is part of its catalytic site. Papain has a molecular weight of 23,406 Da, an isoelectric point of 8.75, and an enzymatic activity temperature of 65 ℃. Glycine, valine, and tyrosine are the three major amino acids (Mitchel *et al.* 1970). The efficacy of the enzyme depends on its origin from the plant, the environmental conditions during cultivation, and the extraction method used. This enzyme is functional within a pH range of 5.0-9.0 and can withstand temperatures of 80 ℃ or 90 ℃ when substrates are present. However, it is rendered inactive and permanently damaged below a pH of 2.0, and it remains stable in urea-containing solutions at concentrations of about 8 M (Júnior *et al.* 2022).

In dermatological applications, the primary function of papain is medicinal, aiding in tissue debridement and accelerating the healing process of burns and wounds (Merck 2023). Papain reduces the pH in the wound bed, which inhibits the growth of harmful bacteria by stimulating the release of cytokines promoting cellular replication (Falanga 2002). It contains anti-inflammatory, bacteriostatic, and bactericide properties in addition to debriding and speeding tissue healing (Osato *et al.* 1993; Owoyele *et al.* 2008). Papain can increase collagen degradation by boosting MMP-1 levels and lowering TIMP-1 when the TIMP- 1/MMP-1 ratio decreases. The lowered TIMP-1/MMP-1 ratio classified collagenase or MMP-1 function as elevated because its inhibitor, TIMP-1, was repressed by papain. These findings show that the application of 3% papain gel can promote the healing of cutaneous wounds in mice by decreasing the local inflammatory response, stimulating angiogenesis, and improving collagen deposition organization. The papain component primarily acts to soften and exfoliate keratin on the epidermis.

Bromelain is a purified extract of the pineapple plant (*Ananas comosus L.*) containing a variety of proteolytic enzymes along with phosphatases, glucosidases, peroxidases, cellulases, glycoproteins, and carbohydrates (Feijoo-Siota & Villa 2011). This enzyme is present in various parts of the pineapple, including the stem, fruit, leaves, and peel, but is most abundant in the stem (EC 3.4.22.32), and in the fruit (EC 3.4.22.33) (Júnior *et al.* 2022). Bromelain, a protease, is extracted from the fruit and stem of pineapples (*Ananas comosus*). Stem bromelain contains several thiol endopeptidases and other components from the stem, bark, and leaves of *Ananas comosus*. Its molecular weight is 35 kDa, its isoelectric point is 10, and its optimal temperature for enzymatic activity is 37℃ (Chaurasiya & Umesh Hebbar 2013; Ferreira *et al.* 2011). The three major amino acids are alanine, glycine, and aspartic acid (Arshad *et al.* 2014).

Bromelain is used in the cosmetic industry to treat wrinkles, dry skin, and acne. It breaks down proteins in dead skin cells, allowing younger skin cells from the lower layers to replace them. Additionally, bromelain helps reduce post-injection bruising and swelling. Bromelain's ability to debride skin burns may be advantageous for early skin grafting (Maurer 2001). Because of its antibacterial properties, bromelain is a possible protease that may be used therapeutically to treat acne. Bromelain demonstrated beneficial effects in mitigating UV-induced cell death and increasing TNF-α mRNA expression. The investigation suggests that bromelain has a more significant protective effect when used as a pre-treatment rather than a post-treatment approach. Overall, the research indicates that bromelain may effectively protect the skin from UV-induced cell damage. Bromelain also was found to degrade the receptor for advanced glycation end products (RAGE) through its proteolytic activity, thereby reducing the receptor's cell-damaging effects and has anti-inflammatory properties by regulating inflammation.

Ficain, also known as ficin (EC 3.4.22.3), is a protease enzyme extracted from the latex stems of the fig tree (*Ficus carica*). Ficin is classified as a sulfhydryl protease due to the presence of a sulfhydryl group (SH) on its active site, based on its chemical properties. This enzyme is a great exfoliator with enzymatic activity, which also contains antioxidant properties. The optimal temperature for enzymatic activity is 50 ℃, with a molecular weight of 24,294 Da and an isoelectric point of 9.0. Recent findings suggest that ficin has antioxidant and whitening effects on skin cells, indicating its potential as a novel bio-cosmetic substance (Cho *et al.* 2019). Research by Malewicz *et al.* (2022), indicated that ficin may be effective in translating mechanistic studies on the brain processes related to the pruritic and nociceptive actions of cysteine proteases. Furthermore, another research by Baidamshina *et al.* (2020) showed the stability and beneficial effects of chitosan-immobilized Ficin, which suggests that its addition to materials used in wound dressing may improve the effectiveness of antimicrobial treatment and promote wound healing by preventing biofouling.

Photolyase is a promising enzyme belonging to the photolyases/cryptochromes superfamily, a diverse group of photoactive enzymes widely distributed across various life forms (Vierock & Hegemann 2023). Photolyases are monomeric proteins, sized between 50 and 61 kDa, and consist of 450-550 amino acids. They contain two covalently bonded chromophores. Light is essential for the photoreactivation process, which converts enzyme-substrate complexes into DNA repair products (Sancar 1990). Photolyases are ancient flavoproteins present in archaea, bacteria, and eukaryotes. They are active against cytosine dimers and cytosine-thymine dimers generated by UV irradiation, though the latter occurs less frequently (Lucas-Lledo & Lynch 2009).

According to (Wang *et al.* 2015), the DNA repair process mediated by photolyase can be divided into three stages, including (i) recognition, a light-independent process during which the damaged DNA forms a complex with photolyase through the flipping of the CPD or (6-4) Photoproduct into the active site of the enzyme, which contains the Glavin cofactor is completely reduced and the photolyase chromophore. Methenytetrahydrofolate (MTHF), (ii) absorbs a photon from the blue-light spectrum, converting FADH to an excited version of FADH. In this stage, the CPD or (6-4) photoproduct ring is opened by bond dissociation in the dimer radical anion, and electron transfer from FADH to the lesions takes place, and (iii) the removal of repaired DNA from photolyases, which completes the repair process (Brettel *et al.* 2022; Terai *et al.* 2020).

Enzymes such as photolyase, which aid in DNA repair, present a promising alternative to many skincare treatments aimed at preventing or reversing sun damage. Recent advancements in liposome immobilization and nanomaterials have made photolyase more accessible in a variety of commercial products. The enzyme's functionality is sustained even under harsh conditions (Ramírez *et al.* 2021). Photolyase is commonly used in topical creams and sunscreens to protect the skin from harmful UV exposure. Additionally, it is employed in therapeutic treatments for skin conditions like premature photoaging, actinic keratosis, and squamous cell carcinoma (Ramírez-Gamboa *et al.* 2022).

The most frequent antioxidant enzyme with the fastest turnover rate is catalase (CAT, EC 1.11.1.6). This type of enzyme is found in living tissues and is very important in the conversion of hydrogen peroxide to water and molecular oxygen, which is considered to be an essential therapeutic element. Catalase is derived from both endogenous and external sources, and it is present in erythrocytes, for example, and its exogenous sources include cotton, sunflower, and pumpkin (Mahomoodally *et al.* 2022). Various research documented the efficacy of catalase in treating inflammatory and dermatological conditions, including vitiligo (Kostović *et al.* 2007).

5 Conclusion

In conclusion, the use of enzymes as active components in cosmetic products has gained popularity in the beauty industry. Assessing the halalness of these products involves considering the source of the enzymes. To ensure that cosmetic products are halal for Muslim consumers, it is essential to use enzymes sourced from plants, which are considered halal.

Conflict of Interest

The authors declare no conflict of interest.

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