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Physicochemical properties and volatile profile of chili shrimp paste as affected by irradiation and heat

Choon Yoong Cheok [c], Babak Sobhi [a], Noranizan Mohd Adzahan [a,*], Jamilah Bakar [a], Russly Abdul Rahman [a], Muhammad Shahrim Ab Karim [a], Zulkafli Ghazali [b]

[a] Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Radiation Processing Division, Malaysia Nuclear Agency, 43000 Kajang, Bangi, Selangor, Malaysia
[c] Department of Chemical and Petroleum Engineering, Faculty of Engineering, Technology & Built Environment, UCSI University, Lot 12734, Jalan Choo Lip Kung, Taman Taynton View Cheras, 56000 Kuala Lumpur, Malaysia

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A B S T R A C T

Chili shrimp paste (CSP) is an exotic traditional Southeast Asian condiment prepared using mainly fresh chilies and fermented shrimp paste (*belacan*) which attributed to strong pungent fishy odor. This study aims to evaluate the effectiveness of electron beam irradiation (EBI) exposure on CSP for microorganisms decontamination, and its physicochemical qualities changes. Changes in capsaicinoid contents and volatile compounds were analyzed using HPLC and GC–MS. Mesophilic bacteria, yeast, mold and pathogenic *Enterobacteriaceae* decreased as irradiation dose increasing from 0 to 10 kGy. EBI at 10 kGy effectively decontaminated the samples with no significant effects on phenolic and capsaicinoids contents compared to the fresh samples. From 24 compounds, irradiated CSP retained 23 volatile compounds, while thermally treated CSP has only 19 compounds. EBI at 10 kGy is effective for decontamination in CSP with lesser destructive effect on volatile compounds and texture compared to thermal treatment.

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1. Introduction

Food can be preserved using several methods. Thermal treatment is a conventional method to use to preserve food. However, this method had a negative effect on physicochemical and sensorial properties of food product. Hence recently, irradiation was employed to eliminate molds, yeasts, pathogenic microorganisms and bacteria to preserve and prolong self-life of food products (Lung et al., 2015). The application of irradiation treatments is classified into three levels based on dosage. Low-dose treatment (<1 kGy) is mainly for insect disinfestation, delay in fruit maturity, and prevention of germination. Intermediate-dose treatment (1–10 kGy) is to eliminate microbial contamination and extend shelf-life of foods and commodities, while high-dose (10–60 kGy) is used to irradiate food prepared for medical patients with a low levels or lack of immunity and astronauts (Lung et al., 2015).

Irradiation treatment has been widely used in the control of mold and mycotoxin in food and feed (Calado, Venâncio, & Abrunhosa, 2014). In particular, it is an effective preservation technique for food that has short shelf-life such as mushroom (Fernandes, Antonio, Oliveira, Martins, & Ferreira, 2012). Its control of *Salmonella* and *Listeria* in shrimp and shrimp products were highlighted (Norhana, Poole, Deeth, & Dykes, 2010). Besides the effects of EBI on microorganisms decontamination by damaging the metabolism via breakage the DNA structure, and denaturation of enzymes and membrane proteins of microorganisms (Lung et al., 2015), its effect on the physical, chemical and nutritional properties of foods also a concern by many researchers. Therefore, studies have been conducted to investigate the irradiation effects on physical, chemical and nutritional properties of food products despite microorganism decontamination. EBI has been evidenced having decontaminating ability while maintaining most of the chemical and antioxidant properties of dried wild mushrooms (Fernandes et al., 2015). However, Gámez et al. (2014) revealed that e-beam irradiation treatment on tomato products increased the antioxidant abilities and z-lycopene content, but a reduction of the *all-E*-lycopene content was observed.

Since CSP is a processed food with a combination of various ingredients, it is important to have a proper preservation to ensure its quality and shelf-life. Hence, the objectives of this study were (i) to determine the acceptable level of irradiation dose in reaching good levels of decontamination in CSP and (ii) to evaluate and compare the chemical and physical qualities of CSP including

* Corresponding author.
E-mail address: noraadzahan@upm.edu.my (N. Mohd Adzahan).

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peroxidase activity, total phenolic content, capsaicinoids contents, textural, color, and volatile compounds among the CSP in the forms of fresh, thermally processed (optimum point), and irradiated (selected dose).

2. Materials and methods

2.1. Chili shrimp paste preparation, irradiation and thermal treatments

Chili shrimp paste samples were prepared by mixing ingredients of 55% red chili (*Capsicum annum*), 14% bird's eye chili (*Capsicum frutescence*), 17% fermented shrimp paste (*belacan*), 7% sugar, 2% salt (2% salt plus the salt content of *belacan* together made 4.4% salt in the final product), 4% calamansi juice and 1% citric acid. All ingredients were bought from a local wholesale market. The stem of the chilies was removed. Chilies and calamansi were soaked in water for 10 min and drained. Calamansi were cut into half and the juice was squeezed manually from the fruits. The fermented shrimp paste was toasted in an oven (ST-2, SALVA, Spain) at 180 °C for 25 min. All ingredients were ground using milling machine (Super mass colloider, Masuko Sangyo, Japan) in 120 μm gap size between two parallel stone plates, with the bottom plate rotating at 1500 rpm. All the ground ingredients were mixed thoroughly using a mixer (HS20 Sakura spiral mixer, Good and Well, Malaysia) for 10 min and the chili shrimp paste (CSP) was ready for irradiation and thermal treatments.

CSP sample was filled manually in 10 g multi-layered (pet12/pe20/al7/pe20/ldpe40) (Vempac, Malaysia) sachets (3.5 × 7.5 × 1 cm) for non-thermal irradiation treatment. Sachets were sealed using an impulse sealer (Arrow ARSH-300, Perniagaan Timbang Dan Sukat Ban Hing SB, Malaysia) and were kept at 4.0 °C until irradiation. Samples were irradiated on the same day of packaging. CSP samples were irradiated using single beam exposure (EPS 3000) with accelerated voltage of 2.0 MeV and beam currents of 1.0, 2.0 and 3.0 mA, at seven different doses of 2.5, 5.0, 7.5, 8.0, 9.0, 9.5 and 10.0 kGy. Sachets were irradiated from larger side to provide less thickness (1 cm) for the electron beam to pass through. The irradiation treatment is conducted in Malaysian Nuclear Agency (Bangi, Selangor, Malaysia) at ambient temperature (25 ± 1 °C).

Three kilograms of CSP were heated for 21.6 min at 80 °C in an electrical steam jacketed kettle (TDB/6-10, Groen, Illinois) for thermal treatment. CSP consists of chunky chili pieces that make it unsuitable to process in a continuous plate or tube heat exchanger. Thus, a batch thermal process in laboratory scale was done in a jacketed and steam sealed tank. The paste was heated in an electrical steam jacketed kettle (TDB/6-10, Groen, Illinois) equipped with three vertical stainless steel blade mixers with dimensions of 80 mm in radius, 25 mm in height, 1.0 mm in blade thickness and a 9 mm in hub radius. The vane mixer was derived by a motor (RW20.n S2, IKA Works Asia, Malaysia) at a speed of 130 rpm. The top of the kettle was covered with a stainless steel plate, while the plate was kept cool by a plastic ice bag to prevent the moisture loss during the process. Approximately 3.0 kg of CSP was processed in each batch. Then, CSP was filled manually into 10-g multi-layer (pet12/pe20/al7/pe20/ldpe40) (Vempac, Malaysia) sachets with the dimensions of 3.5 cm × 7.5 cm × 1 cm while it was hot. The sachets were sealed immediately using an impulse sealer and cooled under convection condition to reach ambient temperature (25 ± 1 °C).

2.2. Quality evaluations

2.2.1. Microbial analysis

Microbiological evaluation of CSP was carried out immediately after irradiation and thermal treatments. An aliquot of 10 g of samples was aseptically homogenized with 90 ml sterile peptone solution (1.0% w/v neutral peptone) in a glass bottle by manual shaking for 30 s. Serial dilutions (1:10) of each homogenized sample were made and plated on plate count agar (Merck, Germany) for total mesophilic bacteria, dichloran rose bengal chloramphenicol agar (Oxoid, England) for yeast and mold, and eosin methylene blue agar (Merck, Germany), which prepared by pour-plating technique, for pathogenic Enterobacteriaceae. One millilitre of the dilution was mixed with molten (45 °C) medium and incubated for 5 days at 30 °C for yeast and mold, and 2 days at 37 °C for total mesophilic bacteria and pathogenic Enterobacteriaceae. Colonies were counted and the results reported as log colony-forming units (CFU) per gram of sample. All plating was performed in duplicates to ensure accuracy.

2.2.2. Peroxidase activity assay

Peroxidase activity was determined as described by Schweiggert, Schieber, and Carle (2005) with some modifications. Aliquots of 50 g of CSP sample were homogenized in a blender (HGBTWTS3, Warning Commercial, USA) with 150 ml of chilled (+4 °C) 50 mM citrate-phosphate buffer (pH 6.5) at a low speed for 2 min for enzyme extraction. Two millilitres of the homogenates were filtered through a nylon membrane syringe filter (0.45 μm mesh size /25 mm diameter). The filtered samples were kept on ice until assay. Aliquot of 0.2 ml of enzyme extract was added to 1.3 ml of 50 mM chilled citrate-phosphate buffer which containing of 12 mM tropolone (Merck, Germany) and 3.3 mM H_2O_2 in a test tube for enzyme activity determination. The tube was vortexed for 10 s in 3000 rpm and the absorbance of yellow product increment was measured at wavelength of 418 nm (Molar extinction coefficient = 2075 L mol^{-1} cm^{-1}) at every 15 s for 3 min. Enzyme activity was reported as nanokatal (nkat) unit (1 Kat is the amount of enzyme that converts 1 mol of substrate per second).

2.2.3. Total phenolic content assay

An aliquot of 30 g sample was mixed with 60 ml of ethanol (95%) in a capped glass bottle. The mixture was homogenized using shaker (M65820, Thermolyne, USA) at 300 rpm for 10 h at room temperature (25 ± 1 °C). The mixture was allowed to stand for 1 h, then 1 ml of supernatant was transferred to a test tube and diluted with 9 ml of ethanol. The mixture was mixed thoroughly using vortex mixer for 15 s in 3000 rpm. Total phenolic content was determined using the Folin–Ciocalteu method as described in a previous work done by Villarreal-Lozoya, Lombardini, and Cisneros-Zevallos (2009). One millilitre of the diluted extract was mixed with 5 ml Folin–Ciocalteu reagent (1:10 diluted with distilled water). After 5 min, 4 ml aqueous Na_2CO_3 (1 M) was added and mixed thoroughly using a vortex (3000 rpm) for 15 s (Na_2CO_3 solution was heated up to 50 °C before mixing). The mixture was kept in dark for 1 h. The absorbance was measured colorimetrically at 765 nm using a spectrophotometer. Total phenolic content was calculated using gallic acid calibration curve (0, 4, 8, 20, 40, 80, 120, 160 mg/L) which has been prepared earlier and expressed as milligram of gallic acid equivalents (mg GAE/100 g dry mass).

2.2.4. Analysis of capsaicinoids content using HPLC

An aliquot of 10 g CSP was mixed with 40 ml of acetonitril (HPLC grade) in a capped glass bottle. The mixture was homogenized using a shaker (M65820, Thermolyne, USA) at 300 rpm for 10 h at room temperature (25 ± 1 °C). The mixture was allowed to stand for 1 h, then 1 ml of supernatant was filtered (using cellulose membrane syringe filter 0.45 μm mesh size/25 mm diameter) and diluted with acetonitril (HPLC grade) to 10 ml in a test tube. The diluted mixture was mixed thoroughly using a vortex for 15 s at 3000 rpm before injection to HPLC to determine the contents of capsaicin, dihydrocapsaicin and nordihydrocapsaicin.

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