LITERATURE REVIEW: FOOD PROCESSING IN MINIMIZING CHEMICAL CONTAMINATION OF RHODAMIN B IN SHRIMP PASTE AND CHLORPIRIFOS RESIDUE IN FRESH VEGETABLES GARNISH WHICH ARE CIRCULATING IN THE COMMUNITIES IN INDONESIA

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Abstract

Introduction: Food circulation among communities is prone to chemical contamination. The contamination is obtained from both food processing and food cultivation (planting, raw materials). One of the examples related to chemical contamination can be seen in the contamination of rhodamine B on Terasi. Although there is a prohibition on using Rhodamine B compounds in food add-ons, which is listed in Regulation of Ministry of Health of Republic Indonesia No.722/Menkes/Per/IX/1988, its usage is widely found. Similarly, chlorpyrifos pesticide residue in lalapan is the other example provided. The usage of it remains to continue even though the result of pesticide residue value is under BMR SNI 7313:2008. The article aims to study food processing efforts in minimizing the chemical contamination of Rhodamine B in shrimp terasi and chlorpyrifos residue in the lalapan vegetables in the communities in Indonesia. A literature review on scientific publications was undertaken through Google Scholar, ResearchGate, Neliti, ScienceDirect, LIPI, Directory Open Access Journal, and Crossref. The keywords used were related to rhodamin B on terasi, synthetic dyes on terasi, natural dyes for terasi, vegetable pesticide residues, Chlorpyrifos residue on vegetables, and how to reduce chlorpyrifos residue in vegetables. All of them were published between the 2015 – 2020 period.

Discussion: Chlorpyrifos residue in vegetables can be reduced by washing, soaking brine, and boiling. The usage of rhodamine B on Terasi can be replaced by the application of dragon fruit skin extract and angkak (red yeast rice) for natural dye alternatives. Conclusion: Washing food with running water and soaking it in hot water before food consumption can lower chlorpyrifos residue level in dark vegetables. However, it is more significant to lower the residue level through the boiling step. The use of natural pesticides can be used as the choice of alternative. Moreover, rhodamine B on terasi can be replaced with natural dye alternatives such as angkak (red yeast rice) and dragon fruit skin extract.
INTRODUCTION

Human beings have the most underlying primary need: food. It has been included in human rights for each human being by the essential mandate of Indonesian law. Good food can form a good quality of human resources, found in the Law of the Republic of Indonesia Number 18 year 2012 about Food (1). Therefore, it should be noted that good food is a food with good nutritional content, safe or free from harmful contaminants that can affect health conditions. Good food can be characterized as a safe food that avoids adverse contaminants: biological contaminants, chemical contaminants, and physical contaminants (2). Biological contaminants are contaminants sourced from living organisms that exist in the environment and can cause damage to food, such as Salmonella bacteria, Fungi Aspergillus, Taenia Saginata parasite, and HAV virus (3). Chemical contaminants are derived from the material or chemical element. Some examples of the chemical contaminant occurrence are the accumulation of metals in aquatic products and dissolved food equipment layers. They occur due to a lack of flushing during washing food equipment used with chemical cleaners (3-4). Physical contamination occurs when foreign objects (that are not the compositional ingredients of food) are intentionally or inadvertently mixed or contained in food by humans or animals. These foreign objects are often found mixed in foods such as gravel, stick, stapler, and hair (3).

Food contaminations are divided into four types: microbiological contamination (bacteria, fungi, fungi, and viruses); chemical contamination (fertilizers, pesticides, mercury, cadmium, and arsenic); physical contamination (hair, dust, and soil; and radioactive contamination: alpha beam radiation and gamma rays) (5). Food can be contaminated, deliberately, or not, during the cultivation and processing process. Such contamination provides local to systemic toxic effects for reversible or irreversible bodies (6).

Toxic effects due to a xenobiotic are varying, depend on the physical properties of xenobiotic chemicals, target organs, mechanisms of action, dosage, frequency of exposure, and vulnerability of biological systems (6). Nevertheless, in some studies that have been published as listed in Table 1 (vegetable) and Table 2 (shrimp Terasi) in the past five years, chemical contaminations are remain found, contaminating food circulation in the communities in Indonesia. Both food commodities derived from the water and agriculture are prone to chemical contamination. Shrimp terasi is fermenting food from these waters and included in people’s food consumption patterns in spices. terasi is generally made from the main ingredients of small fish and shrimp rebon (7). The process of terasi is through several stages: fermentation, milling, and clothesline process that is undertaken approximately 20 days. The addition of salt into terasi products has a function as a preservative (8). Some terasi products have a brownish-black color and are given other dyes; thus, they change to resemble red color (9). The addition of these colors generally uses the synthetic dye of Rhodamine B found in unbranded and packaged terasi products (7).

Rhodamine B belongs to cationic dyes. This dye’s characteristics are crystalline powder, reddish-green or reddish-purple, unscented, and dissolvable, making a solution becomes fluorescent red (10). The addition of mixed ingredients as food addictive is regulated in the Regulation of Ministry of Health of Republic Indonesia No.722/Menkes/Per/IX/1988 about Food Additives. It has been regulated that the use of rhodamine B compound as a food coloring is prohibited. Nevertheless, the results study in Makassar year 2017 showed that the sales of terasi 60% positive rhodamine B with concentrations of 11.8119,05 ppm (7). Moreover, the other study in 2019 stated that 7 out of 10 terasi samples tested provide rhodamine B results with a concentration range of 11.97-98.33 mg/kg. The comparison between shrimp terasi products packaged without brands and packaged using brands, rhodamine B is flat — on average, it is more common in terasi products that are marketed without a brand (71.87> 26.44 mg/kg) (11).

The prohibition of rhodamine B usage in this food is partly due to the toxic effects affecting liver organs and cancer. Furthermore, large doses of exposure in the short term cause acute symptoms such as poisoning (7). The chemical properties of rhodamine B and the heavy metals contained in it are things that threaten human health. The compound chlorine (CL) as heavy metal in rhodamine B is a high-risk, reactive halogen compound. If ingested and enter the body, other compounds will be bound by chlorine compounds since chlorine compounds attempt to meet their body’s stability point, thus threatening the body since it is toxic (12). Besides, toxicity in rhodamine B has also been tested in mice through intravenous injections and acquired a value of LD₅₀ of 89.5 mg/kg along with signs of several symptoms: an enlargement of liver organs, kidneys, and lymphatic accompanied by anatomical changes in organ enlargement in tested animals (11).

In contrast, vegetables from agricultural commodities were also found to have chemical contamination on the use of organophosphate chlorpyrifos pesticide residues. Research in farmers year 2019 showed that 7 out of 10 farmers used chemical pesticides to control Plant Pest Organisms (PPO) (13).
Indonesian farmers, approximately 22.29%, frequently imitate the use of insecticides of organophosphates (14). Pesticides made from active chlorpyrifos are considered quite potent in eradicating insect pests; thus, 75% of farmers use active pesticides as an alternative (15). Meanwhile, pest control and eradication are undertaken through an integrated pest control system (IPM) (16). In principle, plant safety facilities and methods do not rule out humans’ health or safety, nature, and the environment. Therefore, these three things are not threatened (17). The implementation of layoffs has not taken place maximally. The opt-control method currently uses pesticides as the primary choice due to the considerations that provide more benefits: potent, appropriate, and efficient. The assessment is more critical for farmers than any other crop protection technique in preventing crop loss (18).

The dosage and mixing of several pesticides used if they do not comply with the specified requirements can allow the emergence of risks that are detrimental to health, including disorders of the nervous system in the balance of the body (19), acute to chronic poisoning, pests will become resistant to pesticides, and a polluted environment (18). The chlorpyrifos pesticide is included in the type of insecticide in the organophosphate group, namely the ester of phosphoric acid or theophoric acid. As a mosquito repellent, including acute toxicity invertebrates, its effect is through bound systemic acetylcholinesterase to inhibit nerve impulse distribution. As a result, acetylcholine hydrolysis cannot take place (20). Obstacles can arise not only in a matter of hours but over in a week according to the type of anticholinesterase (21). Potentially carcinogenic in case of chronic poisoning. The insecticide mechanism of the organophosphate group is the same as that of carbamate; the spread of nerve impulses is inhibited by acetylcholinesterase.

The near-irreversible bonding of the pesticide cholinesterase and organophosphate makes it very risky. Cholinesterase activity in a depressed state or lag due to absorption is sometimes excellent, but the specific symptoms have not been seen. The appearance of uncertain or vague symptoms such as headaches, nausea, body weakness, chest pain, and others is the effect of cholinesterase action, which shrinks to 60%. In general, neurological symptoms and abnormalities occur after resistance to more than 50% of cholinesterase action (20). According to WHO, a cholinesterase decrease of about 30% from standard concentration indicates that organophosphate exposure has already taken place, so farmers must stop to rest (21).

The results of the chlorpyrifos and Profenofos toxicity test on tilapia in 2015 showed that the LC50 for each exposure gave an average value of chlorpyrifos 3.6 times lower than profenophos. Therefore, the level of toxicity of each insecticide is different in the test biota. The LC50 value in tilapia’s test biota shows that chlorine compounds’ content is more likely to make chlorpyrifos insecticides more toxic than Profenofos. The Food and Agriculture Organization (FAD) states that the LD50 of oral profenofos rats is 358 - 1,178 mg/kg body weight and chlorpyrifos 229 mg/kg body weight that lower levels of chlorpyrifos can kill 50% of test animals. In conclusion, chlorpyrifos has more substantial toxic power than Profenofos (23).

As shown in Table 1 and Table 2, chemicals still contaminate some food commodities of agricultural products and waters from some articles’ findings. The steps were taken by the first perpetrators of the food production chain, such as using chemicals in the process of cultivation, processing, and circulation in the society in Indonesia, provide toxic effects for living things and the environment. Our manuscript aims to analyze how to process food to minimize chemical contamination of Rhodamine B in terasi by using potential natural dyes and residual levels of chlorpyrifos in vegetables with basic techniques before consuming and utilizing vegetable pesticides can be undertaken by producers to consumers.

DISCUSSION

Residue of Pesticide Chlorpyrifos in Lalapan Vegetable

Generally, this vegetable is served or consumed naturally, as a companion to the main menu or garnish. Vegetables are beneficial for the body’s health since its vitamin and mineral content plays a role in regulating its physiology. Vegetables should always be involved in human consumption, although only in a few amounts. Even though the body cannot digest it, its rich fiber supports the peristaltic motion of the intestine and the process of digesting food (24). However, food processing behavior before consumption should be considered to maintain the benefit of its vitamins and minerals. Based on the results of scientific publications summarized in Table 1, the use of chemical pesticides of the organophosphate type of chlorpyrifos remains the most alternative used by farmers.

The use of pesticides is highly beneficial, especially in agriculture, yet it was overused and emitted excessive residue. Plants exposed to pesticides can absorb the ingredients in pesticides and then carried on to harvests called pesticide residues and into the human body if consumed. In other words, the use of pesticides...
leaves residues that are derived from the composition of pesticides themselves and originate when the roots in the soil undergo the absorption process, mostly tuber-type plants. Levels of pesticide residues in the soil will be affected by the properties of the soil. Pesticides from organophosphate groups such as chlorpyrifos are still allowed for residues left in the soil by the applicable regulations. Chlorpyrifos pesticide residues can last long enough in the soil for about 60 to 120 days, and some even last about two weeks to more than a year, depending on climate and other conditions (14).

Some types of vegetables have residual levels of pesticides under BMR when laboratory testing is conducted. In Table 1, the results of chlorpyrifos pesticide residues with or without treatment based on BMR are obtained. High rainfall at these farms can affect decreased levels of chlorpyrifos pesticide residues. Chlorpyrifos will be attached to the surface of leaves and fruit only; thus, rainwater can wash those parts. After treating with pesticides for about 1 - 2 hours on the plant, 40% of the deposits have likely been lost due to washing rainwater; the rest is decomposed by ultraviolet light (25).
Although the residual level of chlorpyrifos pesticide is below the BMR, it does not rule out a person experiencing health problems if exposed to the agent continuously. Therefore, as consumers and farmers, the subsequent efforts can reduce the residual content of chlorpyrifos pesticide in vegetables.

**Lalapan Vegetable Washing**

The easiest, cheapest, and most reasonable method for everyone to significantly lower pesticide residues in vegetables and agricultural products is by washing them with running water for 5 minutes and decreasing the residual value of pesticides. While washing with running water, pesticide residues underwent a hydrolysis process. Water volume, water pH, and pesticide levels are important factors during this process. Besides, pesticide residues trapped by dust grains attached to agricultural produce can be removed by the washing process. Each pesticide has different characteristics or physical properties of the chemical; thus, it can decrease levels (26).

It is different from the characteristics of some pesticides that are not readily soluble in water, which means that if they were washed using plain water, the residual content would decrease only in a small amount. Washing agricultural products with 2% brine could reduce grape chlorpyrifos residues by 44-79% (26). Washing techniques using brine are arguably preferable to dissolving the laundry with a lemon, tap, tamarind, or baking soda water.

Liquid detergent formulated only for washing fruits and vegetable results in a more significant reduction in residual levels. Research in vegetable lettuce that was containing profenofos insecticide residue when not washed has a level of 0.204 ppm while washing with water will make the residual content in lettuce amounting to 0.080 ppm, and the residual content in lettuce is even more significant when washing using a special liquid detergent used for that much vegetable, as 0.061 ppm. It can be concluded that the profenofos levels of pesticide residues decreased by 70.1% (27). The pesticide properties of the organophosphate group, which are readily biodegradable, affect the decomposition of the decrease in pesticide residue levels; however, the dose used and pesticide spraying duration during the planting period to harvest also affect the amount of shrinkage of pesticide residue levels (25). Therefore, washing vegetables correctly and properly before processing is vital to reduce residual levels for consumers who eat them unprocessed, such as *lalapan* vegetables.

**Immersion with Hot Water and Boiling**

Hot water can be one of the efforts to lower pesticide residues in plants because of several pesticide groups’ sensibility. Shrinking or disappearing residues of this pesticide can result from degradation in hot water treatment (26). The best results in terms of texture, taste, color, and decreased residual levels can be obtained with 10 minutes of immersion and 5 minutes of boiling (28).

Soaking and boiling using hot water in agricultural products are useful to reduce the levels of pesticide residues. One of which is the organophosphate insecticide group, chlorpyrifos. The effort was undertaken using hot water as a technique for soaking agricultural products and boiling, leading to reduced organophosphate pesticide residues, including chlorpyrifos, by 52 - 100% (26).

However, if this treatment is carried out without paying attention to the length of treatment, it can impact the value of vitamin C in agricultural products. The decrease in the value of vitamin C content occurs due to the oxidation process, considering that vitamin C has properties at risk of being easily damaged and oxidized (28). Moreover, heat rays, alkalis, and oxidizers can speed up the oxidation process. It should also be noted that all treatments must pay attention to the dominant location of pesticide spraying, for example, on cabbage. The part that is often exposed to pesticides is the outer petals or croquettes, so it is better if the outer part is peeled and then treated with washing, soaking with hot water, or boiling.

**The Use of Active Charcoal**

Agricultural waste produced by farmers is often abundant yet frequently discarded without being reused. Waste, such as rice husks, coconut shells, and others, are often thrown away. The waste can be used in lower levels of pesticide residues derived from insecticides such as aldrin, linden, dieldrin, DDT (organochlorine group), chlorpyrifos, and diazinon (organophosphorus group), as well as carbofuran insecticides (carbamate group) of about 70 - 90%. The decreasing method is undertaken by warming up the waste at 500°C within 5 hours and using an electric furnace at about 900°C for about 60 minutes for activation. Microbes such as degraded soil bacteria and nitrogen-binding bacteria are very fond of active charcoal cavities as a place to live. Thus, pesticide residues left on the inside of the active cavity are slide into C and N nutrients, thus increase both bacteria. Degrading microbes will later decompose incoming pesticide residues or entangled in the inside of the active charcoal cavity. Active charcoal can absorb
high pesticide residues (expressed through LOD numbers) with 460.4 mg/gs and 1191.8 mg/gs (26).

Basil as a Vegetable Pesticide

Using organic pesticides as an alternative in controlling OPT by some farmers is not familiar and not practical. A study in Wombo Mpanu Village in 2019, a wide-range against some red onion farmers who used pesticides, obtained the fact that as many as 3 out of 10 farmers used organic pesticides as an OPT control method shallots (13). Some farmers have sufficient knowledge about plant pesticides’ potential in crops, but that knowledge is less supported by the knowledge of plant species selection and some types’ control of OPT (29).

Plants that can be processed as ingredients for the manufacture of vegetable pesticides are very diverse. One of them can be found on basil. Basil is included in shrubs and has a distinctive aroma. On the sides of the leaves and basil flowers contain high citral; thus, it can secrete a distinctive aroma. Then, the flowers and their glucans produce seeds that basil uses for the breeding process. Basil fruit that has seeds with ciniri black and dry color indicates the seeds have been cooked. The seeds on the basil flowers cooked on the stem are useful for obtaining seeds (30).

Most people know basil only as a garnish or vegetable. The content of essential oils in basil can be used as vegetable pesticides. The active ingredients such as eugenol and cineole in basil leaf essential oil can act as larvae, and juvenile hormones prevent the development of mosquito larvae Anopheles aconites (26). Phenol absorption (eugenol) on the skin works as a poison when the larva’s body surface is in contact.

This essential oil pesticide has advantages, such as the breadth of spectrum in biological activities, non-toxic, able to adjust, systemic, not tricky in degradation, and has a safety level than synthetic chemical pesticides. However, there has also a side of weakness in terms of the characteristics of essential oils that tend to be volatile and not durable with sunlight. The effectiveness of pesticides from essential oils is more synthetic and slow. Therefore, it is necessary to add other chemical compounds to the pesticide formula made from active essential oils to overcome the weakness whose properties can improve the active ingredient (30).

Rhodamine B in Terasi

The distribution of terasi with rhodamine B is still found among people in Indonesia. terasi is sold without special packaging in traditional markets, containing chemical contamination, such as rhodamine B (7,31). The traditional market is easy to reach by the estranged producers of a small home industry with a license. Hence, consumers need to be more observant and wiser in deciding to buy a food product. Although physical or organoleptic observations are subjective, we still need to be suspicious and aware. terasi product has an original blackish-brown color (32). The color does not look beautiful for the consumers.

Meanwhile, food color has its impression and becomes an essential part of showing the acceptance of a food product (8). Thus, this is the background of many manufacturers in giving Rhodamine B to its core products as a gap in providing the colors. It aims to make the consumers are interested.

Extract of Dragon Fruit Skin

Dragon fruit’s skin has anthocyanin content that has a function to provide natural color substances. The anthocyanin content of the pink dragon fruit (Hylocereus polyrhizus). Its skin extracted amounted to 26,4587 ppm (32). Thus, skin extraction can be used as another option to replace synthetic colors, and it will be safer for health. The natural pigment content of dragon fruit skin can be used as an alternative; thus, doubts about health’s adverse impact can be eliminated (33). Study in 2017 about the difference between the concentration of dragon fruit skin and the color of shrimp rebon, the increase in red color occurs after extracts from dragon fruit skin and can improve the appearance of terasi (32).

The administration of high concentration affects the low value of terasi intensity (34). The cause is the increased concentration of beet color. It increased the intensity of the terasi red color. Visually, terasi tend to have a natural color of dark brown even without the use of colors. The original color of terasi will appear more dominant when the red color fades on terasi. Compared to red color, brown color can absorb more light and cause the brightness to be smaller. Therefore, the decrease in brightness value in terasi products is influenced over the time of fermentation. It can be added at a 40% concentration to get the right red color because it gives tangible results to discoloration and has got the highest product acceptance rate in terms of appearance tested to 30 semi-trained panelists as samples (32).

Rosella Extract

The use of rosella flowers as a natural color that is added for food is not worked enough. The source of anthocyanin pigments can be produced by rosella. In addition to anthocyanins, rosella also has calcium and vitamin C content that is beneficial in the reduction of hypertension, antiseptic gastrointestinal tract, and
antioxidants. *Kalik’s*, commonly known as rosella petals, is an edible part. There are flavonoids gossypetine, hibiscetine, and sabdaretine in the dried rosella of the petals (35). The content of flavonoids called gossypetine, hibiscetine, and sabdaretine works as antioxidants, which can fight free radicals (36).

The difference in concentration is given when the addition of rosella extract turns out to have a noticeable effect on the color of the shrimp *rebon terasi* (9). The color level in the shrimp *rebon terasi* follows the high concentration of rosella extract given. The addition of a high concentration of rosella extract will make the color of *terasi* become increasingly dark yellowish red. Conversely, if the concentration is given in small amounts, then the shrimp *rebon terasi* will be bright yellowish-red. In the treatment with a 5% concentration, it is an organoleptic test that got the best value and was liked by panelists. It also has the best quality. Thus, the concentration of rosella extract of 5% added can give more exciting color to *terasi* and can be used as an alternative to replacing synthetic colors.

**Angkak**

Another natural color that can be used is angkak. *Angkak* has been used in China for centuries. *Angkak* comes from the fermentation process of rice with *Monascus sp.*, generally using *M. purpureus*. Through the fermentation, *angkak* reduces secondary metabolites in the form of natural pigments, two primary pigments that are red by monascorubramin and rubropunctamine (37). The resulting natural pigment has anthocyanin content that serves as an antioxidant (38). Toxicity tests of their use of *angkak* in food showed that it is relatively safe. Pigments produced by the *M. purpureus* is not toxic to the body and does not cause immune disorders (39). *M. purpureus* has an adequate level of stability and is safe in its use for food add-ons (40).

Temperature, duration of heating, sunlight, pH, and oxidizer affect the stability of the number’s color. The form of powder *angkak* has a more level of stability than the *angkak* with the form of concentrated liquid (concentrated). *Angkak pekatan* has a red color that stability in sunlight is about 91.7%, while the *angkak* in powder form is about 96.0%. Also, the manufacture of shrimp *terasi* by utilizing *angkak* as a natural color was recommended to obtain natural coloring can add *angkak* as much as 0.5% and the addition of *angkak* with a content of 1% or more has a function to lower the number of bacteria and block the growth of time.

**Salt Concentration**

The color of shrimp *terasi* in organoleptic testing preferred by consumers is shrimp *terasi* with high salt concentration. In her research, the added salt content of 15% gave the best coloring results. Salt levels affect the amount of astaxanthin value and AW value in the production of shrimp *terasi*. The high salt content can provide astaxanthin value and low AW value, so the activity of PPO enzymes is inhibited and has an impact on the reclamation of little browning also (8). The content of astaxanthin has a noticeable effect on shrimp *terasi* with the addition of salt to the processing process. Astaxanthin content is only found in *terasi* that uses shrimp as the primary ingredient of its manufacture. Astaxanthin is a carotenoid pigment of crustaceans and aquatic organisms, such as shrimp (41). Shrimp as fermented food can produce red color due to astaxanthin’s role in its skin (8). The bond of astaxanthin on the shrimp body derived from other detached elements makes a red color on the shrimp *rebon terasi*; hence, astaxanthin is free to form. Enzymes from bacteria and the body of shrimp will help in the process of release. Protease enzymes cause a free natural pigment release reaction to protein bonds that form pink, red, to orange (42).

Not only that, but the process of clothesline can also be another factor that affects the brightness value of *terasi* products. The product discoloration caused by the clothesline process makes the color darker. The clothesline stage can result in a darker appearance of *terasi*. During the clothesline, oxidation mechanisms can no longer be avoided; thus, the browning process occurs (32).

**CONCLUSION**

Pesticides of the organophosphate group have characteristics that are readily soluble in water, so processing vegetables by washing makes residues left behind easily lost. For vegetables that have skin such as glue (wax) more significantly performed by soaking hot water. The use of *angkak* can be used as a replacement for Rhodamine B, and the process of clothesline affects the color results on the shrimp terasi.

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