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Effects of Steam Pretreated Rice Biomass Condensate Containing Soluble Solid Inhibitors on Disruption of *Pomacea Canaliculata* Egg

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ABSTRACT

Pomacea canaliculata is an invasive freshwater snail species that has become a serious pest of rice in irrigation and paddy fields and is popularly known as the golden apple snail. They are species that are capable of surviving and spreading rapidly, causing significant changes in the ecosystem. The application of natural by-products of a physicochemical method of biomass steam pre-treated condensate is one option for disrupting Pomacea Canaliculata egg. This experiment was conducted to investigate the feasibility of steam pre-treated rice biomass condensate which contained soluble solid inhibitors as a biopesticide to eradicate Pomacea canaliculata. Rice straw, rice husk, and a combination of rice straw and rice husk (1:1) were pre-treated by the saturated steam pre-treatment in a batch reactor at high temperatures (190°C and 210°C) for 10 min. The steam condensate produced from this system was analysed for major degraded products or inhibitors such as furfural, hydroxymethylfurfural (HMF), and phenol. The steam condensate which contained soluble solid inhibitors was then analysed for solubility test on P. canaliculata eggs. The effect of soluble solid inhibitors on the eggs was structurally examined by using a scanning electron microscope (SEM). The results revealed that rice husk which was pre-treated at 210°C reflected the highest contents of furfural (0.300 g/L), HMF (1.670 g/L), and phenol (0.087 g/L). However, the combination of rice biomass sample (1:1) condensate at 210°C demonstrated the greatest solubility percentage (11.51%) when treated to the eggs P. canaliculata eggs. The image of the egg structure examined by SEM clearly displayed the fractures forming on the cuticle layer of the eggs. SEM results demonstrated that the condensate from saturated steam pre-treated rice biomass has the possibility to be used as a biopesticide to disrupt the eggs and eventually could prevent the snails' invasion.

Keywords: Steam pretreatment, Autohydrolysis, Biopesticide, Rice biomass, *Pomacea canaliculata*

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1. INTRODUCTION

Lignocellulosic biomass (LCB), such as wood, agricultural, and forest residues are highly potential economical feedstocks because of their limitless availability, sustainable generation, less intensive agricultural management, and positive environmental effects (Stupak *et al*., 2021; ORNL, 2005). There are about 90% (dry weight) of plant materials that are composed of major polymers - cellulose, hemicellulose, and lignin (Yat *et al*., 2008) along with minor amounts of pectin, protein extractives, and ash (Bajpai, 2005). These LCBs are rich in energy from sugar sources, but the accessibility of sugars is hindered by physicochemical, compositional, and structural factors. Pre-treatment is the best approach to enhance the accessibility of cellulose. Basically, the main purpose of pre-treatment is to breakdown the lignin and hemicellulose structure, disrupt the crystalline structure of cellulose, and increase the porosity of lignocellulosic materials (Kumar *et al.,* 2009; Mosier *et al.,* 2005). There are several pre-treatment methods, including physical, physicochemical, chemical, biological, and combination of methods (Mosier *et al.,* 2005). Despite pre-treatment can enhance the feasibility of cellulose, some pre-treatment parameters can lead to the generation of lignocellulose-by products which are inhibitors for downstream processes. An example of LCB treated by autohydrolysis under high temperature can cause the degradation of sugars (pentoses and hexoses) into by-product formations, such as furfural and hydroxymethylfurfural (HMF). Other inhibitors are phenolic compounds which are mainly derived from lignin (Jönsson & Martin, 2015). Autohydrolysis is a physicochemical process that treats LCB with only water, and provides a simple, low cost and environmentally friendly pre-treatment technology to produce sugars from agricultural and municipal wastes (Tan *et al.,* 2008; Vegas et *al.,* 2008; Garrote *et al.,* 1999; Lee *et al.,* 2009). The LCB is heated in water at a temperature range of 130°C — 230°C (Lee *et al.,* 2009).

In Malaysia, the third most abundant LCB source is contributed by rice cultivation of about 2.37 MT which generates two major wastes, such as rice straws and rice husks (Goh *et al.,* 2010). One of the major concerns of rice cultivation issues in Malaysia is the spread of *Pomacea canaliculate* which is the only freshwater snail listed amongst the 100 worst invasive species (Lowe *et al.,* 2000). The combination of several factors, such as feeding habits which is primarily focused on young stem and leaves (Salleh & Arbain, 2015) and the capability to eat 7—24 seedling per day (Halwart, 1994) with high fecundity and unusual characteristics of their eggs, lead to the successful establishment of their population in invaded areas (Dreon *et al.,* 2014). There are many control strategies recommended by the Department of Agricultural (DOA) Malaysia, including cultural management, physical, chemical, and biological (Salleh *et al.,* 2012). Despite all control strategies, the population of *P. canaliculata* is still uncontrollable and remains the main invasive pest that causes huge damage and loss to the farmers. Most farmers prefer to use chemical molluscicides due to their fast and effective results, nonetheless they can cause adverse effects on the environment and farmer's health (Salleh *et al.,* 2012). Regarding this issue, there were several research conducted to utilise 'green' technology to exterminate the population of *P. canaliculata.* Lately, 'green' technologies became a great interest amongst researchers due to their characteristics, such as minimisation or elimination of by-products production and the use of organic solvents and toxic reagents that are hazardous to the environment and human health (Armenta *et al.,* 2008). Generally, this research aimed to use a 'green' technology by introducing the steam pre-treated rice biomass condensate which contained soluble solid inhibitors as a biopesticide to eradicate *P. canaliculate.* The specific objectives of this study are to synthesise soluble solid inhibitors from rice biomass by saturated steam autohydrolysis pre-treatment method, to determine the concentration of the inhibitors in the steam condensate, and to investigate the solubility and feasibility of steam condensate on *P. canaliculate* eggs.

2. EXPERIMENTALS

2.1 Preparation of Rice Biomass

Rice biomass used in this study were rice straw and rice husk. Rice straw was collected from paddy fields after the harvesting season and rice husk was collected from a local rice mill factory. Biomass was ground to reduce their size (~0.3 mm). The ground rice biomass was sieved to remove the impurities and obtain a uniform particle size of the sample.

2.2 Collection of Eggs of *P. canaliculata*

Fresh *P. canaliculata* eggs were harvested from the local paddy fields and irrigation located in Perlis, Malaysia. The eggs were stored in an incubator made from a plastic container which was modified to imitate the natural environment to preserve the eggs. The eggs were left in the incubator for three days before the solubility test was done.

2.3 Saturated Steam Pretreatment (Autohydrolysis)

Steam pretreatment was conducted by using a batch reactor with a capacity of 500 cm^3. Samples used were rice straw (RS), rice husk (RH), and the combination of rice straws and rice husks (RS+RH) in the ratio of 1:1. Ten grams of ground sample was placed in the sample holder at the top part of the reactor. The reactor was filled with 100 cm^3 of water to leave a volume of gap or space for a steam generation when water is heated up to the set temperature. When the water boiled and turned into steam at temperatures above the boiling point of water, the reactor was deaerated for 10 s, allowing the air to escape through the vent valve. In a closed vessel, the temperature was controlled and ramped to saturated steam temperature. As the water temperature increased, its vapour pressure also increased. In this experiment, the saturated steam conditions attained were recorded and referred to the steam table. The biomass was treated by saturated steam autohydrolysis at two different high temperatures (190°C and 210°C) for 10 min. The timing set for steam pretreatment begun when the target or set temperature was reached. After the desired residence time was completed, the reactor was immediately lifted out of the furnace and cooled by interaction with cold water. The steam condensate that remained in the chamber was collected for analysis of soluble solid inhibitors and solubility test on *P. canaliculata* eggs. All the condensate samples were stored at 4°C before analysis.

2.4 Determination of Hydroxymethylfurfural (HMF)

HMF was determined according to the original method (White, 1979) with a slight modification. Sample of 1ml was diluted in 25 ml of distilled water in a 50 ml volumetric flask. The sample was clarified by 0.5 ml of Carrez Solution I (150 mg/ml of potassium ferricyanide) followed by 0.5 ml of Carrez Solution II (300 mg/ml of zinc acetate). Distilled water was added to the flask to the mark. The solution was filtered, and the first 10 ml was discarded. Five ml of the filtrate were mixed with 5 ml of 0.2% sodium bisulphate solution. The mixture was centrifuged well before being measured for absorbance at 310 nm.

2.5 Determination of Furfural

Furfural was measured according to the original spectrophotometric method (Khabarov *et al.,* 2006). The test reagent was prepared by dissolving 4 g of mercury (II) acetate in 200 ml of distilled water and adding with 5ml of glacial acetic acid to prevent hydrolysis. About 1ml of the sample with 5 ml of test reagent in a 50 ml volumetric flask was mixed. The mixture was diluted with distilled water to the mark. Then, 1ml of this solution was an aliquot and mixed with 0.3 ml of concentrated sulphuric acid in a test tube and incubated in a boiling water bath. After 30 min of incubation, the solution was transferred into a 100 ml volumetric flask and was diluted with distilled water to the mark. The absorbance of the solution was measured at 238 nm.

2.6 Determination of Phenolic Compounds

The concentration of phenol was specified by the reaction of phenolic compound with 4-aminoantipyrine (4-AAP) in the presence of potassium ferricyanide at pH 10 established by United States Environmental Protection Agency (1978). The reagents used were 2% of 4-AAP solution and 8% of potassium ferricyanide solution. One ml of diluted sample was added to 2 ml of ammonia buffer solution and 2 ml of 4-AAP. Then 2 ml of potassium ferricyanide was added and mixed well. The solution was incubated at room temperature for 15 min before the absorbance was measured at 510 nm.

2.7 Solubility Test on Eggs of *P. canaliculate*

A solubility test was performed on Day 4 (age of the eggs). Approximately 1000 µl of the condensate from each sample was placed on the eggs drop by drop to be absorbed into the eggs by using a 100 µl micropipette. The treated eggs were then placed in the modified plastic container or the breeding chamber (165 mm × 225 mm × 80 mm) which was previously filled with tap water to provide a humid condition. Their solubilities were observed and recorded. The weight before (initial weight) and weight after the solubility test (final weight) were recorded. Then, the eggs were left in the incubator or breeding chamber. The solubility was expressed in percentage and calculated by using Equation 1.

$$\frac{\text{Final weight} - \text{Initial weight}}{\text{Weight of liquid condensate}} \times 100\% \quad (1)$$

2.8 SEM Analysis

SEM analysis was conducted by using Joel JSM-6460LA, Japan on Day 9 after incubation. The selected sample was based on the highest solubility. The specimen was coated with titanium by using a sputter coated. Then the specimens were scanned with the magnification of 100x, 500x, 1000x, and 5000x.

3. RESULTS AND DISCUSSION

3.1 pH and Soluble Inhibitors Contents of Condensate

The value of pH during the autohydrolysis was a vital indicator for the pre-treatment severity (temperature and time) and the hemicellulose solubilisation that allowed the recovery of carbohydrates in soluble mono and oligosugars (Carvelheiro *et al*., 2004). From Table 1, it can be seen that the temperatures of the pre-treatment had significant influence on the acidity of condensate. The pH values at both temperatures for all biomasses were in the range of acidic values between pH 2.89 and pH 3.67. RS under pre-treatment at 210°C had the highest acidity (low pH value) which was 2.89. The decline in pH value in the condensate was associated with the increments in acid concentrations of either acetic or formic acid, as well as other various acids generated. According to Garrote and Parajó (2002) and Lee *et al.* (2010), acetic acid was produced from the cleavage of acetyl ester which was naturally present in the hemicellulose of the biomass. The hydrolysis of hemicellulose underwent dehydration, leading to the formation of the uronic acids, while formic acids were formed from the further degradation of HMF and furfural (Jönsson &Martin, 2015). This mechanism occurred under high temperatures and long residence time conditions. In addition, the processes, such as water autoionization and ionisation of acidic species (acetic acid, formic acid, and uronic acid) led to the production of hydronium ions which further catalysed a series of autohydrolysis reactions (Garrote *et al*., 2001; Garrote *et al.,* 2002). According to Bianchini *et al.,* (2022), variations in environmental pH did not cause statistically significant mortality or avoidance behaviour in *P. canaliculata* at the analysed times and the final survival

rates were 100% under the influence of pH 4–pH 9. Table 1 also shows the contents of inhibitors which are furfural, HMF, and phenol.

Table 1. pH and inhibitor contents of the condensate

Biomass	Temperature (°C)	pH	Content of the Inhibitors (g/L)		
			Furfural	HMF	Phenol
RS	190	2.89	0.044 ± 0.005	0.071 ±0.02	0.015 ±0.003
	210	3.35	0.040 ± 0.005	0.078 ±0.017	0.063 ±0.004
RH	190	3.05	0.073 ±0.013	0.229 ±0.043	0.043 ±0.011
	210	3.16	0.300 ±0.094	1.670 ±0.740	0.087 ±0.016
RS+RH	190	3.67	0.012 ±0.007	0.118 ±0.147	0.008 ±0.009
	210	3.11	0.029 ±0.005	0.118 ±0.02	0.011 ±0.008

It was obvious that the temperature significantly influenced the content of the inhibitors. Biomass treated at 210°C showed a higher content of the inhibitors as compared to at 190°C. Rice husk treated at 210°C had the highest contents of all inhibitors which were 0.3g/l, 1.67g/l, and 0.087g/l for furfural, HMF and phenol, respectively. Amongst the inhibitors, HMF was the major product followed by furfural and phenol. HMF resulted from the degradation of hexose sugars, such as glucose, galactose, rhamnose, and mannose. This result was parallel with the high contents of hexose sugars originated from cellulose and hemicellulose part of LCB (Jönsson & Martin, 2015; Ertas *et al.,* 2014; Nabarlatz *et al.,* 2007). Whereas, the degradation of pentose sugars, such as xylose and arabinose which derived from the hemicellulose part of LCB, led to the formation of furfural (Jönsson & Martin, 2015). Lignin can be regarded as a rich source of phenols. Chemically phenolic compounds were structured as a hydroxyl group bonded to an aromatic ring (Ozdal *et al.,* 2013). The acidic condition of the treatment led to the splitting of acid-labile linkages in lignin macromolecules which generated phenolic compounds in the condensate. Some examples of phenolic compounds that can be derived from lignin were coniferyl, aldehyde, ferulic acid, and 4-hydroxy benzoic acid (Jönsson & Martin, 2015). Phenolic compounds were also derived from xylooligosaccharides in the hemicellulose part. This is because, a part of lignin was covalently bound to xylan and phenolic acid, whereby ferulic acid appeared in the side chain of heteroxylan of cereals (Nabarlatz *et al*., 2007).

3.2 A Solubility Test on the Eggs of *P. canaliculata* and Morphological Structure After Test

All of the condensates tested on *P. canaliculata* eggs showed positive results in the solubility test which could absorb or penetrate the egg masses as shown in Table 2. The steam of pre-treated mixed rice biomass with 0.158 g/l of soluble solid inhibitors (0.029 g/l of furfural, 0.118 g/l of HMF, and 0.011 g/l of phenol) and pH 3.11 at 210°C showed the highest solubility percentage (11.51%). The liquid condensate of steam pre-treated RH at 210°C exhibited the highest of 2.057 g/l soluble solid inhibitors with pH 3.16 and showed a 5.54% solubility percentage, which was reduced by about half. Based on the solubility test results (0.44% – 11.51%), the soluble solid inhibitors compounds were feasible to be selected for further study to suppress the hatching of the eggs surface layer. Furthermore, they acted as the biopesticide and inhibited the egg growth by killing the embryo.

Table 2. Solubility percentage test on *P. canaliculata* eggs for 4 days

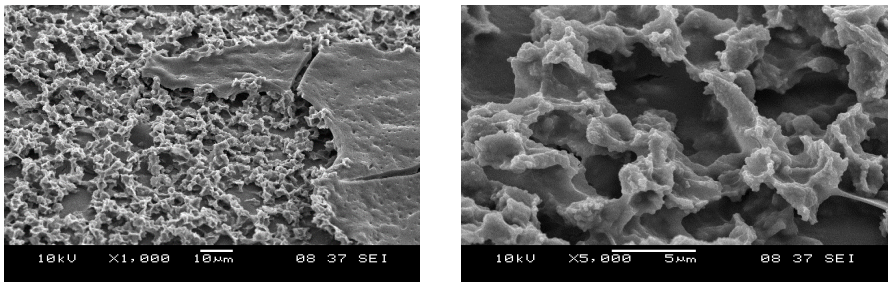
Types of Rice Biomass	Temperature (°C)	Solubility Test (%)
RS	190	3.86
	210	6.21
RH	190	0.44
	210	5.64
RS + RH	190	3.57
	210	11.51

Figure 1 shows the morphological structure of the controlled and treated *P. canaliculata* egg with liquid condensate which contained soluble solid inhibitors (RH: RS; 210°C steam pre-treatment) on Day 9. The application of soluble solid biomass condensates to the egg age in between 3 and 9 days (Salleh & Arbain, 2016) was intended to observe the hatchability of the egg after certain development of the embryo. Unfortunately, none of the eggs in masses hatched until Day 9 might be due to other factors, such as the conditions of stored eggs or eggs being dead when taken out of the rice fields. However, major differences in morphological observations were shown, whereby majority of disruption happened on the treated eggs with soluble solid inhibitors.

The untreated eggs had a solid structure of smooth layers with no cracks or openings. It was obviously seen that there were fractures on the layer of the treated eggs. One of the fractures that occurred might be from the phenol compound of liquid condensate affected the insolubility of the cuticle layer of the eggs. Phenols in the condensate acted on the layers of eggs by protein-phenolic interactions. The potential mechanism of the protein-phenolics compound could be hydrogen bonding interaction, hydrophobic and hydrophilic interaction, ionic bonding interaction, covalent cross-linking interaction, and Van der Waals forces (Ozdal *et al.,* 2013). The interaction of phenol with protein caused changes in physicochemical properties of protein, such as solubility, thermal stability, and digestibility (Labuckas *et al.,* 2008; Rawel *et al.,* 2001). Basically, protein molecules are heterogenous unbranched chain of amino acids. This chain then undergoes the protein folding process, a highly complex process, whereby the proteins folded into their biochemically three-dimensional functional shapes. This process was strictly determined by amino acid sequence and the polarity differences of the side chain of the protein. Primarily, the chain folded in a way that most of the non-polar (hydrophobic) side was inside of the protein while the polar (hydrophilic) side was on the outside (Albert *et al*., 2002). When protein was exposed to the organic hydrophobic solvents, the hydrophobic effects would occur. The interaction of the hydrophobic interior of the protein with the hydrophobic solvents caused the events of unfolding or denaturing of the protein conformation (Blokjizl *et al.,* 1993).

In this study, phenolic compounds might be the denaturing agent for the protein of the egg layer by solvating the hydrophobic interior side of the protein. In most cases, phenolic type significantly affected the protein-phenolic interactions (Seczyk *et al*., 2019) and the reciprocal interactions between phenolic compounds and proteins resulted in various nutritional, functional, and structural changes on both sides (Yilmaz *et al.,* 2022). Therefore, this mechanism reaction led to the formation of fractures on the layer as can be observed in SEM images (Figure 1). The fractures layer could provide a gap or pathway for the condensate to be absorbed into the eggs. In the eggs, furfural or HMF could react on the living embryo and led to its death. This was because furfural and HMF (Capuano & Fogliano, 2011) is known for their possible toxicological effects, such as carcinogenicity, mutagenicity, cytotoxicity, and genotoxicity.

A. The morphological structure of controlled *P. canaliculata* egg on 1000X and 5000X magnification.



B. The morphological structure of treated *P. canaliculata* Egg by liquid condensate containing soluble solid inhibitors (RH:RS; 210°C steam pretreatment) on 1000X and 5000X magnification

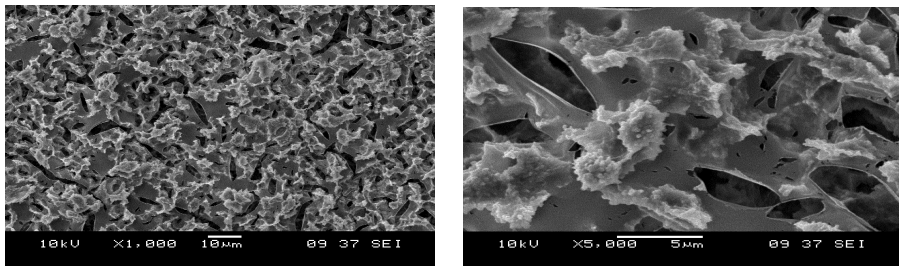


Figure 1. The morphological surface structure of fresh *P. canaliculata* eggs (A) and treatment by liquid condensate (B) under SEM

The employment of pre-treatment technology of rice biomass can create zero waste systems in the rice production cycle. The main concept of a zero-waste system is that the products and processes are designed and managed to avoid and eliminate waste and recover all its resources from the waste stream (Zaman & Lehmann, 2013). By applying the soluble solid inhibitors from the pre-treated rice biomass, the sustainability of the rice production cycle could be achieved. The wastes are enhanced and utilised to be formulated as biopesticide, which in turn could contribute to the pest control, and thus the increase in the rice production volume.

4. CONCLUSION

In this study, steam pre-treatment of rice husk at 210°C showed the highest level of all inhibitors produced. However the mixed rice biomass (RS: RH) pre-treated at 210°C has the best level of solubility into the eggs of *P. canaliculata* which might reflect to be the best combination of soluble solid inhibitors content. The formation of the fractures proves that the soluble solid inhibitors have a potential to attack and inhibit the growth of eggshells and the embryos. Thus, some further research and development need to be done on the optimum concentration of inhibitors that give the best result with minimum or no adverse effects on farmer`s health and environment, the hatchability of the eggs, the mechanism reactions of the inhibitors on the embryos and the eggs, and the formulation and commercialization of the condensate as a biopesticide.

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