Effectiveness Of Rice Husk Charcoal As Bioadsorben In Absorbing Heavy Metal Lead (Pb) On Freshwater Snail Meat (*Pomacea* sp.)

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ABSTRACT
This research was aim to identify the effectiveness of rice husk charcoal as a bioadsorbent in absorbing heavy metals Pb in freshwater snail meat (*Pomacea* sp). The main material used was adult fresh water snail with body weight of 80-120 g/head obtained from the swamp waters of Banjar Regency, South Kalimantan. Bioadsorbent was used as much as 10% and 15% with a duration of contact on freshwater snail meat 6, 12, 24, 48 and 72 hours. Analysis of Pb métal content using Atomic Adsorption Spectrofotometry (AAS) instrument. The results showed that : (1) the use of rice husk charcoal as a bioadsorbent was able to reduce the levels of Lead (Pb) in freshwater snail meat (2) duration of contact of 24 hours with the use of rice husk charcoal as much as 10% and 15% was could reduce lead (Pb) in freshwater snail meat from 20,444 mg/kg to < 0.001 mg/kg with 99.99% absorption effectiveness. The used of rice husk charcoal on freshwater snail meat increased the pH of freshwater snail meat from 5.5 to 7.8 at 10% used and 8.03 at 15% used, respectively.

Keywords : *Effectiveness, rice husk charcoal, bioadsorben, Pb, freshwater snail meat*

1. INTRODUCTION

South Kalimantan has an area of 3,737,743 hectares with a geographical condition of some tidal swamps and 100,000 hectares of flooded areas. This area is a potential habitat for the growth and development of freshwater snails [1]

Freshwater snails can live up to 2-6 years with a life cycle of ± 60 days and high fertility [2]. Generally live-in ponds, swamps, rice fields, irrigation, waterways and areas that are always flooded. Freshwater snails contain nutrients that are needed by poultry, namely as a source of animal protein because they contain high enough protein in the range of 50-60%, breed fast, can live in extreme environments, poor in oxygen, metal polluted waters, and various cropping conditions soeating machenis due to the pattern of his life can eat for 24 hours a day [3].

Although the protein content of freshwater snails is equivalent to that of fish meal, freshwater snails cannot replace fish meal because of their low digestibility. One of the causes of low protein digestibility of freshwater snails in the body of freshwater snails contains heavy metals that blocking the absorption of nutrients in poultry. Snails are a group of molluscs that obtain food by filtering food in their habitat (filter feeders). As a result of this way of life, snails have the potential to accumulate heavy metals such as Pb. Lead metal is non-biodegradable and can accumulate in living organisms [4,5]

The body of the freshwater snail containing heavy metals Pb 55 ppb and Cd 28 ppb [6]. Absorption of lead (Pb) and mercury (Hg) in the snail's body had an

absorption effectiveness of 99.9% and Pb ranged from 0.56-0.98 ppm [7,8] . The higher the concentration of heavy metals in the water, the more metals will accumulate in the snail's body. Lead (Pb) is a dangerous metal that can cause toxic effects for poultry if it accumulates continuously and is difficult to clean. Freshwater snail processing by means of boiling at 100 ° C for 20 minutes is one way to minimize the danger of heavy metals in addition to lowering but boiling heavy metals Pb and Cd can also reduce nutrients such as Ca and protein decrease 15.70% and 22,29% [6].

Based on these considerations, it is necessary to find an alternative to adsorb heavy metals in freshwater snails. One method is using rice husk charcoal activated. Charcoal is a porous solid containing 85-95% carbon, produced from materials containing carbon by heating at high temperatures. The adsorption process is carried out by contacting the solution or solid so that the metal component is absorbed on the surface of the solid pore [9]. Rice husk activated charcoal was chosen because it is easier to obtain, contains polysaccharides in the form of lignin, cellulose, silica and hemicellulose which have the ability as adsorption [10]. The use of rice husk charcoal is mostly used in agriculture to improve soil structure, increase soil fertility, increase soil pH and eliminate pathogenic bacteria. Rice husk charcoal is still not commonly used in the livestock sector, especially in poultry farming with the aim of eliminating pathogenic bacteria. Rice husk charcoal was using as an additive in feed for laying hens as much as 1% for 8 weeks was able to reduce ammonia gas from 52% to 39% and improve the performance of laying hens [11]. Supplementation of 1% rice husk charcoal was reported [12] in feed was able to reduce triglycerides in blood plasma and *Escherichia coli* and *salmonella* in feces. The use of rice husk charcoal as a toxic absorber in poultry feed is still rarely used, especially in freshwater snail meat. There is no specific information on the effectiveness of absorption of heavy metals, especially lead (Pb). The purpose of this study was to identify the effectiveness of rice husk charcoal as a bio adsorbent in absorbing heavy metals Pb in freshwater snail meat (*Pomacea* sp).

2. MATERIALS AND METHOD

2.1. Materials

Adult freshwater snail with a body weight of 80-120 g/head obtained from swamp waters in Banjar Regency, South Kalimantan. Rice husk charcoal obtained from charcoal processing in Landasan Ulin-Syamsudinnoor District, Banjarbaru City, South Kalimantan, Aquades, . Concentrated HNO_3, Pb standard solution (1000 g/mL), 95% H_2SO_4 and 20 mL 5% $KMnO_4$ (w/v). Hydroxylamine hydrochloride 10%, $HClO_4$ solution : HNO_3 (2:1) AAS (Atomic Absorption Spectrometer) Shimadzu 6800AA, ZZKD magnetic stirrer, oven, 100 ml measuring cup, volume pipette, analytical balance, 100 ml volumetric flask, funnel, spray bottle, 250 ml erlenmeyer, spatula, furnace, bunsen, 100 mesh sieve, electric blender and filter paper.

Table 1. Chemical composition of rice husk charcoal

Component	Composition
pH	7.8*)
Dry matter (%)	94.61*)
Fixed Carbon (%)	16.20*)
Calsium oxide(CaO) (mg/kg)	935.719*)
Silika oxide (SiO2) (%)	40.64*)
Lignin (%)	37.87**)
Cellulose (%)	39.67**

Description: *) Materials tested at the Baristand Laboratory, Banjarbaru City, South Kalimantan

**) Materials were tested at the Laboratory of Nutrition and Animal Feed, Lambung Mangkurat University, Banjarbaru

2.2. Method

Rice husk charcoal production The rice husks are first washed using plain water which serves to remove the dirt that is still attached and then dried in the sun for 24 hours for 1 day, then put in an oven at 105^{o}C for 2 hours. This drying process aims to reduce the water content in the rice husks, then the rice husks are roasted in a kiln for 2 hours at a temperature of 300^{o}C, after that the rice husks which have become activated charcoal in solids are then ground to reduce the size. The chemical composition of rice husk charcoal used in this study was presented in Table 1.

2.3. Preparation Of Freshwater Snail Meat

Freshwater snails to be tested for heavy metal content are washed, removed from their shells, cut and then mixed with rice husk charcoal in solid form with a moisture content of 40-50% and stored according to treatment. At the end of the treatment, the freshwater snail meat that had been in contact with rice husk charcoal, was washed using aquadest until there was no more rice husk charcoal left, mashed with a blender/homogenizer until homogeneous, then placed in a clean and covered polystyrene. The implementation stages include ashing, wet destruction using a microwave and reading the calibration curve on the AAS. The working procedures of each heavy metal follow the standards set by the National Standards Agency, namely Pb [13].

2.4. Treatment

The treatments used were the level of use of rice husk charcoal and the time contact of freshwater snail meat with rice husk charcoal, namely: Level of use of rice husk charcoal (X)

P1 = 10%, P2 = 15% (w/w); Duration of contact (Y) T1 = 6 hours, T2 = 12 hours, T3 = 24 hours, T4 = 48 hours T5 = 72 hours

Variables

The content of heavy metals in freshwater snail meat before and after washing with rice husk charcoal, Pb and pH. Determination of the Effectiveness of Metal Absorption [14].

Metal absorption effectiveness

$(EF)=\frac{(Yi-Yf)}{Yi} x\ 100\%$

Yi Where EF is the reduction effectiveness, Yi is the initial metal concentration and Yf is the metal concentration after absorption.

3. RESULTS AND DISCUSSIONS

This study begins with the manufacture of rice husks into charcoal rice husk is used as adsorbent of heavy metals in the freshwater snail meat, which makes the size of the adsorbent becoming smaller 40 mesh and reduce the water content by heating. After that the adsorbent was mixed with freshwater snail meat until homogeneous with a concentration of 10% and 15% of the total material used and stored at room temperature.

3.1. The Effectiveness Of Absorption Of Rice Husk Charcoal On Pb In Freshwater Snail Meat

Based on Table 2. showed that rice husk charcoal have the ability to absorb heavy metals contained in freshwater snail meat. The used of 10% (w/w) rice husk charcoal powder was could reduced the levels of Pb in the freshwater snail meat from 20,444 mg/kg to 5,366 mg/kg with a duration of contact of 6 hours and 1,754 mg/kg with a duration of contact of 12 hours.

Furthermore, the effectiveness of heavy metal absorption of Pb was 73.52% with a duration of contact of 6 hours and 91.42% with a duration of contact of 12 hours. This study showed that the more use of rice husk charcoal powder, namely the use of 15% on freshwater snail meat, the effectiveness of lead absorption (Pb) decreased from 20,444 mg/kg to 8,582 mg/kg with a duration of contact of 6 hours and 4,424 mg/kg, with the effectiveness of Pb absorption were 58.02% and 78.36%, respectively.

Table 2. Heavy metal content, effectiveness and absorption of rice husk charcoal on Pb in freshwater snail meat

	Duration of contact (Hours)					
	Control	6	12	24	48	72
Rice husk charcoal powder 10%(w/w)	20.444	5.366	1.754	<0,001	<0.001	<0.001
Effectiveness absorption (%)	0	73.52	91.42	99.99	99.99	99.99
pH	5.5	6.10	6.24	6.43	6.43	7.80
Rice husk charcoal powder 15%(w/w)	20,444	8.582	4.424	<0,001	<0.001	<0.001
Effectiveness absorption (%)	0	58,02	78.36	99.99	99.99	99.99
pH	5.5	6.26	6.70	7.07	8.30	8.03

Duration of contact, amount of adsorbent and pH are three important variables in the absorption of heavy metals including Pb. The results of this study showed that absorption of Pb in freshwater snail meat was influenced by the duration of contact. The longer the contact time, the more metal is adsorbed because there are more opportunities for activated carbon particles to come into contact with Pb. This is due to the more Pb bound in the pores of the activated carbon. According to [15] the length of contact of metal ions with the adsorbent greatly affects the absorption. The duration contact ie Pb absorption will also increase to a certain extent, it will reach a maximum, then it will decrease again due to the desorption process. This is one of the phenomena in physical adsorption which states that adsorption process was reversible [16]. However, the use of rice husk charcoal as much as 15% turned out to reduce the absorption of Pb in freshwater snail meat. This is thought to be closely related to pH, where increasing the pH value will further reduce the absorption of heavy metals. The results of research by [17] the optimum Pb absorption was at pH 6.

3.2. Effect of the use of rice husk charcoal on the reduction of Lead (Pb) and the effectiveness of the absorption of Lead (Pb) in Freshwater snail Meat

The effect of using rice husk charcoal on the reduction and effectiveness of lead (Pb) absorption in swamp snail meat is presented in Figure 1 and Figure 2. The concentration of metal ions was increased absorption efficiency decreases, because the ability to absorb adsorbents against metal ions were maximum where the decrease in absorption efficiency at high

concentrations occurs because the number of metal ions in solution is not proportional to the amount of metal ions in solution, available adsorbent particles so that the adsorbent will reach the saturation point and the absorption efficiency will decrease [18].

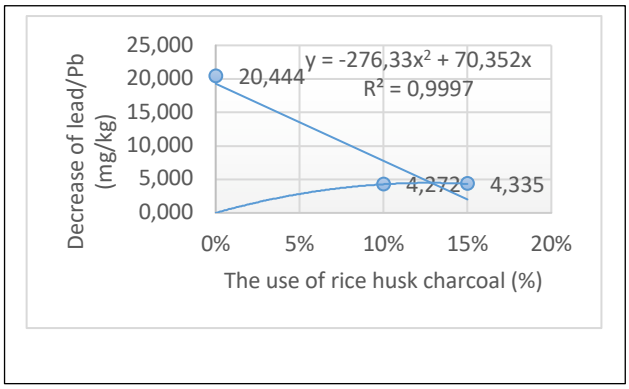

Figure 1. The use of rice husk charcoal to Decrease Pb in freshwater snail meat (mg/kg)

The concentration of metal ions is closely related to the number of active sites on the surface of the adsorbent, which is able to bind the metal, if the number of active sites were large enough compared to the number of metal ions, the absorption capacity will be high. absorption will be constant and even decrease because there has been saturation of the adsorbent. At higher concentrations, the number of ions available to bind in the bonding area of excessive and the driving force of metal ions is getting stronger, thereby increasing adsorption [19]. In addition, the pH factor also plays in the metal reduction process and the effectiveness of metal absorption.

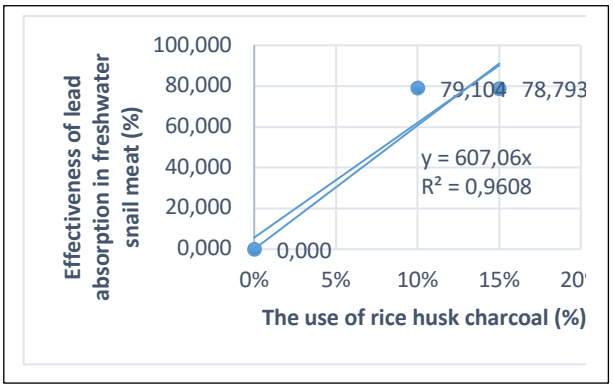

Figure 2. The use of rice husk charcoal on the effectiveness of lead absorption in freshwater snail meat (%).

The results of this study, the higher the use of rice husk charcoal in freshwater snail meat, tends to increase the pH value from 5.5 to 8.3. Pb metal works optimally in an acidic environment, namely at pH 4 [20] the adsorption is relatively high, this can occur because the metal hydroxy complex (MOH^+) formed in the solution is higher and the surface of the adsorbent will be negatively charged by releasing protons so that through the electrostatic force there will be an attraction that causes an increase in adsorption. The reaction that occurs was as following: $Pb^{2+} + 2H_2O\ [Pb(OH)_2]^+ + 2H^+$. Furthermore, at pH 5 and above the adsorption decreased, this happened because at that pH the metal ion Pb(II) began to hydrolyze and $Pb(OH)^{3-}$ were formed, at high pH the surface of the adsorbent is negatively charged, resulting in repulsion between the surface of the adsorbent and metal ion species, so that adsorption is reduced so that the higher the use of rice husk charcoal does not significantly reduce lead (Pb) in freshwater snail meat, alkaline pH conditions, metal ions can form hydroxide deposits so that the adsorption process is difficult to occur [21].

3.3. Effect Duration of Contact with Rice Husk Charcoal on Lead (Pb) Reduction and Effectiveness of Lead (Pb) absorption in Freshwater snail meat

The effect of duration of contact between rice husk charcoal and snail meat on the reduction of lead (Pb) and the effectiveness of lead absorption (Pb) in freshwater snail meat is presented in Figure 3.

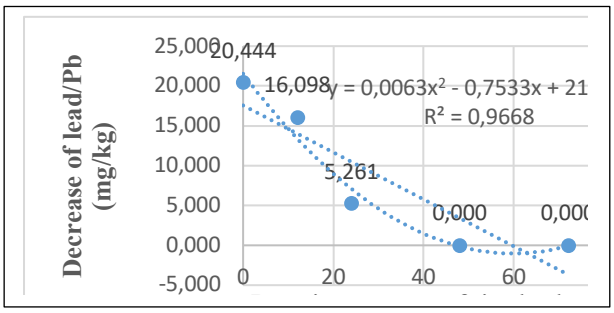

Figure 3. The duration contact of husk charcoal as much as 10% to the decrease in lead metal (Pb) in swamp snail meat

Figures 3 and 4 showed that both the use of 10% and 15% rice husk charcoal was able to reduce lead in freshwater snail meat. The results of this study indicate that duration can reduce lead (Pb) in freshwater snail meat up to and significantly increase the effectiveness of the absorption of the metal.

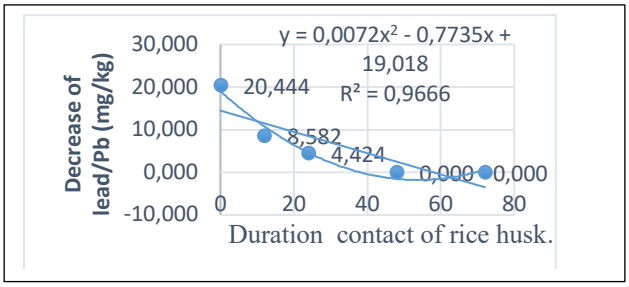

Figure 4. The duration of contact of rice husk charcoal as much as 15% to the decrease in lead metal (Pb) in freshwater snail meat.

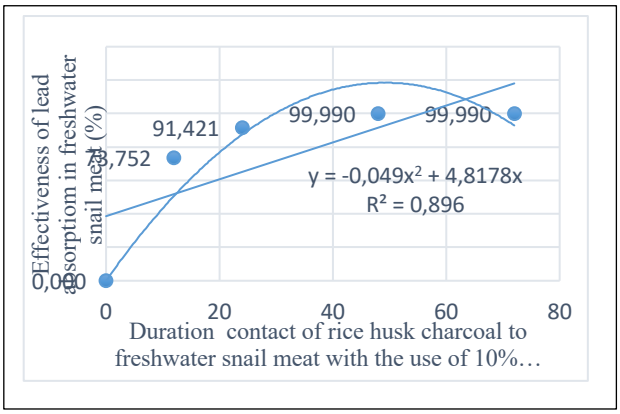

Figure 5. Duration of contact of rice husk charcoal to freshwater snail meat with the use of 10% rice husk charcoal on Effectiveness of lead absorption

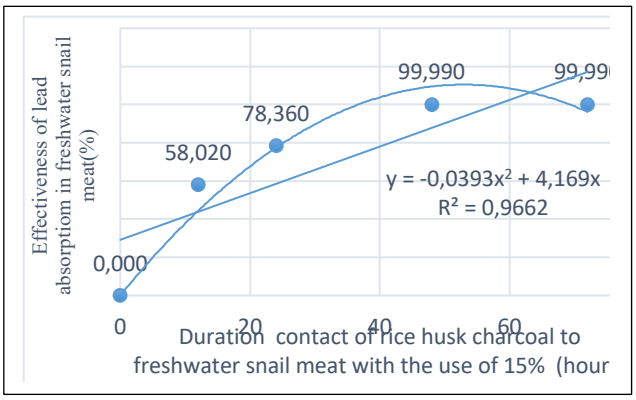

Figure 6. Duration of contact of rice husk charcoal to freshwater snail meat with the use of 15% rice husk charcoal on Effectiveness of lead absorption.

Furthermore, the effectiveness of lead (Pb) absorption in freshwater snail meat is presented in Figure 5 and Figure 6. The longer the duration of contact, the more metal is adsorbed because there are more opportunities for adsorbent particles to come into contact with metals in freshwater snail meat. On the other hand, the longer the duration of contact, the looser the bond in the freshwater snail meat will cause the lead to decrease and the absorption effectiveness to be higher, because the more opportunities for adsorbent particles to come into contact with metal or lead (Pb) contained in the freshwater snail meat [22]. (Salmariza *et al*., 2016). The results of the analysis carried out, the effect of duration of contact on absorption capacity has a linear graphic form.

The results showed that the higher the use of rice husk charcoal caused a decrease in the effectiveness of lead absorption (Pb) in freshwater snail meat. This condition is shown in the use of rice husk charcoal as much as 15%, indicating the effectiveness of lead absorption is lower than the use of 10% rice husk charcoal. This is in accordance with the statement of [23] that the amount of adsorbent weight affects the adsorption process, where at high weight variations there is interference (disruption) between the binding spaces due to agglomeration of the adsorbent, resulting in the active surface of the adsorbent not being completely open to absorb lead (Pb) so that the process absorption is not effective and the removal efficiency is reduced. The indicated was the longer duration of contact allows the diffusion and attachment of adsorbate molecules to take place better, but if the use of rice husk charcoal is increased, it is possible that the condition of the active site is saturated, there will be a decrease in lead absorption capacity in freshwater snail meat. According [24] the increase in the mass of the adsorbent means that it will increase the number of particles and the surface area will be even greater, causing the removal efficiency value to also increase. However, with the increase in the value of removal efficiency means a decrease in adsorption capacity. The decrease in adsorption capacity will result in desorption. Desorption were a condition where when the adsorbent is saturated or close to saturation, the adsorbate that has been absorbed will be released from the adsorbent and return to being an impurity in the sample, thereby reducing the removal efficiency. Futhermore, that under these conditions lead (Pb) will come into contact with the substrate, in this case the freshwater snail meat.

4. CONCLUSIONS

The concluded that be used of rice husk charcoal as a bioadsorbent was could be reduce Lead (Pb) levels in freshwater snail meat. The duration of contact of 24 hours with the use of rice husk charcoal 10% could be reduce lead in freshwater snail meat from 20,444 mg/kg to < 0.001 with 99.99% absorption effectiveness.

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