Utilization of rice husk as a tanning agent in the tanning process of leather (A mini review)

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Abstract. Rice is a food crop which is grown in Indonesia widely and used as a staple food crop for filling domestic food needs. Rice husk is a solid waste that formed from rice grain milling. Along with the increase in national rice production per year, the rice husk also increase. There is silica content in rice husk have a potency that used as a tanning agent. It can be used as a material substitution of chrome sulfate as conventional tanning agent that have carcinogenic properties. This article will explain about tanning process, the potency of rice husk in Indonesia, rice husk utilization, and silica extraction process also nano-silica processing from rice husk. Besides that, it will describe silica and nano-silica usage in the tanning process, mechanism tanning nano-silica and leather properties that produced from the tanning process with nano-silica.

Keywords: rice husk, tanning agent, silica content

1. Introduction

In the process of making leather, the tanning process is one of the key steps to produce good leather. Currently, the commonly used material for tanning agent is chromium sulfate. This is caused the leather produced can be utilized as various skin-based products. However, the use of chromate sulfate also has an adverse effect on the environment because of its carcinogenic property [1]. In the tanning process, 60% of chrome bonds with the skin, and the rest 40% is discarded along with wastewater [2]. This is very dangerous for the living being and the people who live in the surrounding of the wastewater disposal. There are still many leather tanning industries that do not have a wastewater treatment plant (WWTP), and some industries with WWTP are still ineffective in preventing chromium from being discarded along with wastewater. According to [3], chromium in wastewater produced during the tanning process was 3-350 mg/L. According to [4], the content of Cr⁶⁺ in the wastewater of tanning industry was 0.03-2.09 mg/L.

Chromium is discharged into wastewater with a valency of Cr³⁺ and Cr⁶⁺. However, Cr⁶⁺ has toxicity level of 100 times Cr³⁺. Accumulation of Cr⁶⁺ in the organs may damage metabolic functions and also causes carcinogenic, mutagenic, and teratogenic effects [5]. According to [6], the chromium compounds may enter the body in several ways, i.e. through chromium contaminated food, and exposure or direct inhalation. Also, the chromium that enters the body through food has higher concentration compared to that which enters through inhalation or skin contact [7, 8]. This is because the food itself (plants) has been contaminated with chrome. [6] stated that chrome accumulates in each part of the plant. Therefore, certain handling is needed to ensure that chrome does not pollute the environment.

According to [9], there are several types of leather tanning processes, and the tanning agent commonly used is sulfate chromium. But there are other materials that can be used in the tanning process, such as is silica. Silica is a mineral material that can be renewed and is abundantly available in
Indonesia. It is an environmentally friendly material. The ability of silica to stabilize raw skin can reduce the use of chrome in the skin tanning process [10]. Silica tanning by using sodium silicate can increase skin shrinkage temperature up to 65 °C. The increase in shrinkage temperature indicates that silica can bond with collagen in the skin/hide. A smaller particle of silica is needed in order to penetrate the skin better [10], one of the means of which is by making nanoparticle of silica.

2. Tanning Process

Tanning process is the activity of using animal skin/hide waste (raw skin) into leather with higher selling value. This process causes properties changes in skin/hide. Leather is resistant to biological, chemical, physical, and mechanical damage. There are several stages to process rawhide into leather, i.e. beam house, tanning, and post tanning [9].

The objectives of the tanning process are: 1) To stabilize the skin against enzymatic degradation and increase resistance to chemicals. 2) To increase shrinkage temperature and skin resistance to hot water. 3) To increase skin/hide strength characteristics. 4) To increase porosity in skin/hide fiber texture. 5) To reduce the ability of the skin to expand [11]. The purposes mentioned are the impact of the cross-linking between collagen and tanning agent.

The tanning agent commonly used in this process is chromium salt. Chromium salt is easy to obtain, cheap, and it yields good results on the skin. It also can be used in various types of skin articles that will be produced. Chrome penetrate to skin/hide tissue by diffusion and reacts with carboxyl groups in collagen. Inter cross-linking and intramolecular cross-linking produce physical, chemical, and biological stability. This process includes basification by using weak alkaline chemicals to improve the anion properties of the carboxyl collagen groups, and increase the traction to Cr\(^{3+}\), which causes covalent bonds [12]. Figure 1 is a reaction that occurs between chromium and carboxyl groups [9].

![Figure 1. Reaction that occurs between chromium and carboxyl groups.](image)

On the other hand, the use of chromium sulfate as tanning agent causes an increase in BOD and COD in wastewater [13]. In addition, it also causes the residual appearance of chromium in wastewater. It is caused only some part of chrome that bound to the collagen in skin/hide. This case will be very dangerous for the environment, chromium is carcinogenic material.

Chromium is a complex compound that can easily change shape simply by oxidation [14]. Chromium has an oxidation number (-2 to +6), but chromium 6+ and chromium 3+ are the most stable forms in nature [5] and have different biochemical properties [6]. However, both types have different level of toxicity. Cr\(^{6+}\) has toxicity level of 100 times of Cr\(^{3+}\). The presence of chromium in waste of leather
tanning process will endanger living beings, especially humans, as chromium compounds can cause cancer [1].

Some of the measures to prevent chromium pollution were by handling wastewater that has been formed, with flocculation, filtration, coagulation [2, 15, 16], and by recovering chrome from wastewater and solid waste [17, 18, 19, 20, 21, 22, 23]. In addition to these methods, other measures that can be done to deal with the problem of chrome in the process of tanning leather is by combining chrome tanning materials with a more environmentally friendly tanning material or by replacing chrome tanning materials with other tanning material. One of the ingredients that can be used is silica [10, 24, 25].

3. The Potency of Silica in Indonesia
Silica is a renewable and abundant material in Indonesia. In Indonesia, silica can be obtained from rice husk and sugarcane bagasse. Paddy is a food plant which seeds are the staple food source in Indonesia. The seeds of paddy plants are called grains, consisting of husks and rice grains (rice). [26] states that 20% of grain is husk. According to [27], dried paddy rice produced by Indonesia has increased from 2011-2015, from 65 to 75 million tons (Figure 2), making the potential of husks produced from dried milled grain approximately reaches 15 million tons. Thus, the increase in dried milled grain can also increase national silica production. The content of silica in rice husks is 87-97% after the rice husk is processed through perfect combustion [28].

4. Silica Utilization
The use of silica has now developed in various sectors of life. The common use of silica is as an air absorber to prevent high humidity in the environment surrounding the silica. Generally, Silica is used in the form of silica gel. It is used to maintain humidity in shoes, textiles, food, bags, etc. According to [29], silica can be used in various fields such as fertilizers, insulators, insect controllers, adsorbents, as well as catalysts and cement or concrete.

In addition to its utilization as an air moisture treatment, silica is also used in concrete-making mixtures. The use of silica in concrete mixes aims to deal with the crack problem while the concrete is still fresh. Silica addition in a concrete mixture can reduce cracks in concrete [30]. Silica that bonds with calcium hydroxide (its by product) may reduce the gas and water permeability and reduce cracks in concrete [30, 31] and increase the durability of concrete [31, 32]. In addition, the use of silica also aims to reduce the effects of greenhouse gases caused by the cement industry [33]. This industry contributes to CO2 emissions that amount approximately 6-7% per year [34].

In other industries, silica is used as an absorbent of liquid waste [35, 36]. In [35] research, silica gel waste is used as an absorbent of phenol contained in a liquid. Meanwhile, silica gel waste is utilized to absorb cationic surfactants in textile wastewater [36].

Silica is also used as an ingredient in fertilization for plants [37, 38]. This is because silica is a component found in plant cells [39]. The use of silica as plant fertilizer can increase plant resistance to
biotic and abiotic pressures [40, 41, 42], stimulate growth [43], increase resistance to toxic mineral pressures [44, 45] and improve photosynthesis [46, 47].

In the rubber industry, silica is used as a filler in the manufacture of rubber products. This is due to the addition of silica that provides unique properties, i.e. resistant to heat and cold, long lasting when exposed to the atmosphere, and physically inert to the rubber produced. It is also resistant to heat in a wide range of temperatures [48]. The unique properties of silica rubber provide convenience in utilizing the rubber products, one of which is insulator [49, 50, 51], and tires [52].

5. Silica and Nano-silica Extraction Process
Rice husk is a material that contains silica [53]. The content of silica in rice husks increases along with the process of rice husks ashing. The content of silica in rice husk ash is 60-97% [28, 54]. The extraction process of silica from rice husk can be done by the sol-gel method [55]. This extraction method is carried out based on the solubility of amorphous silica in alkaline solutions, such as KOH, NaOH, and Na2CO3. Furthermore, the dissolved silica is precipitated using acids, such as HCl, H2SO4, citric acid, and oxalic acid [28]. This is due to the nature of silica which will form gel under neutral conditions [55]. According to [56], this is also due to the deprotonation of siloxy and silanol groups in a large amount of silica filtrate.

In general, silica from rice husk extraction is nano-silica. The presence of agglomeration causes the size of the silica particles to become large. The process of making nano-silica is carried out by continuing the sol-gel extraction process of silica. After the precipitation process using acid, silica is aged in a few days. The gel obtained was centrifuged and then dried afterward. Furthermore, silica size was reduced to obtain nano size [57, 58].

6. Silica in Tanning Process
In the tanning process, silica becomes an option [12]. Silica in the form of sodium silicate can increase skin shrinkage temperatures up to 65 °C and can reduce the use of chrome in the tanning process. The increase in shrinkage temperature indicates that silica can bind to skin collagen. The bond that occurs is depicted in Figure 3 [10]. Hydroxyde ions in silica will form hydrogen bonds to collagen. It is very different with covalent bonding in chromium tanning. Hydrogen bonding is a weak bond that result low shrinkage temperature to leather.

The use of sodium silicate in the skin tanning process has not completely replaced chrome in the tanning process. In addition, it has the disadvantages of low shrinkage temperature and weak mechanical properties of the skin [59]. To addicting of the bonding that occur between silica and collagen, [24, 25] did nanosilica tanning. It was done to determine the effect nanosilica on leather. According to [10], that smaller size of silica may produce more reaction with collagen. [24] said that addicting nanosilica 1% could keep stability of leather to temperature (Figure 4).
The research showed that the use of nano-silica can increase shrinkage temperature up to 95 °C and have superior physical and mechanical properties compared to chrome tanning (Table 1) [24, 25]. However, before nanosilica tanning process, the pelt was treated by oxazolidine 2%. This temperature increase is due to the nano-silica bond with hydroxyl groups and with -C=N- in arginine, histidine, and tryptophan of collagens. Standart of shrinkage temperature in chromium tanning is 100 °C, [25] reported that a combination of tanning using nano-silica 7% and oxazolidine 2% produced leather with shrinkage temperatures reaching 107 °C (Figure 5).

**Table 1.** Comparison physical strength of crust leather with chromium and oxazolidine – nanosilica.

| Tanning system      | Tensile strength (Mpa) | Extension at break (%) | Tear strength (N/mm) | Burst strength (kg/cm²) |
|---------------------|------------------------|------------------------|----------------------|------------------------|
| Combination tanning | 14.7                   | 83.2                   | 49.6                 | 12.2                   |
| Chrome tanning      | 15.9                   | 78.5                   | 52.5                 | 13.4                   |
| Standart in china   | >6.5                   | 25 – 60                | >18                  | -                      |

pH and nanosilica concentration affects the size of nano-silica size particles during the tanning process. The optimum pH in the nano-silica tanning process is 3-3.5, pH under these conditions will cause agglomeration of nano-silica particles. Meanwhile, the nano-silica concentration during the tanning process is 2% of the weight of pickle pelt. Increased concentration causes an increase in the size of nano-silica particles [24].

Up to date, nanosilica research as a tanning material uses synthetic tetraethoxysilane. In addition, the characteristics of nanosilica used as tanning material are still unknown. Rice husk is a byproduct of rice mills, but it contains silica, which can be used as a tanning agent. According to [28], rice husk is the largest source of silica product (amounted to 87-97% after experiencing perfect combustion). In addition, this method is relatively easy and cheap in cost [60].
Combination tanning can be done to achieve the same shrinkage temperature of leather as chrome tanning. Nanosilica tanning with oxazolidine has been shown to increase shrinkage temperatures reaching 95 °C and 107 °C [24, 25]. However, the result and characteristics of nano-silica single tanning are still unknown in order to produce leather that conforms to the standard, i.e. shrinkage temperatures of 100 °C.

7. Conclusions
Rice husk is a potential waste that can be used as a renewable source of silica. Silica can be utilized as fertilizer, cement/concrete, insulators, and adsorbents. However, silica from rice husk has the potential to be used as an environmentally friendly tanning material too. This is due to the ability of silica in increasing the shrinkage temperature of leather.

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