# Research on the Mechanism of Improving Rice Straw Self-bonding *via* NaOH Solution Pretreatment

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Rice straw pretreated with NaOH can be used to develop a kind of filling material of building walls for a greatly improved self-bonding property. In this work it was shown that NaOH solution can easily destroy the internal tubular structure, thus decreasing the stability of the rice straw. The mechanism explaining effects of the pretreatment measure was examined by analyzing the ash content using scanning electron microscopy (SEM). It was found that the ash content in the rice straw, elements like oxygen, carbon, silicon, can be reduced by the pretreatment of the rice straw with 1% (mass/mass) NaOH solution for 24 h. The thorny structures, spherical protuberance structures, and rod-shaped particles originally attached on the rice straws' surface decreased by 90% after the treatment of NaOH solution. The contact area was correspondingly increased, and the wetting property on the surface was improved. As a result, the "bite force" among the pretreated rice straw surfaces was enhanced, leading to an improvement in self-bonding.

*Keywords: Filling materials of building wall; Rice straw; Self-bonding; NaOH pretreatment*

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## INTRODUCTION

China generated a huge amount of rice straw, and the area harvested of rice occupied 18.56% of the land among the rice-growing region according to the Food and Agriculture Organization of the United Nations in 2017 (FAO 2019). Rice straw is one of the products remaining after rice-harvesting. It is an agricultural waste but also a biomass material, mainly consisting of lignin, cellulose, hemicellulose, and ash. The lignin is insoluble in water. Cellulose and hemicellulose are surrounded by a stable structure (Zhao *et al.* 2019). And most of the ash consists of inorganic matter, distributed on the surface of the rice straw, making the rice straw hydrophobic (Kumar *et al.* 2019). It is necessary to remove these substances during the upcycling of rice straw, but their properties make it hard to do so.

China is a fast-growing developing country with a large population. The conflict between the growing energy requirement and the lack of environmental resources is getting more and more severe in this country. Making use of the rice straw in self-insulating materials for building walls not only can serve as a way to recycle the rice straw and offer comfortable living spaces, but it also offers energy savings and suppresses the air pollution caused by the rice straw burning. Traditionally, the rice straw bales are formed *via* mechanical bundling into large-sized or medium-sized blocks. The buildings made of rice straw bales offer safety, comfort, and environmental protection, which can be easily found even in many developed countries and regions (Lawrence *et al.* 2009; Ashour *et al.* 2011; Thomson and Walker 2014; Lecompte and Le Duigou 2017). However, the traditional rice straw bales are too large in terms of size, which compresses floor space and limits the floorplan's extension. In other words, traditional straw bales are not suitable for Chinese urban residences. Thus, there grows an urgent requirement of small-sized straw blocks in the construction of Chinese cities.

The content of rice straw is determined by the variety and planting area, and most of the rice straw cultivating in south China mainly consists of 32 to 47% cellulose, 19 to 27% hemicellulose, 5 to 24% lignin, and 10 to 17% ash (Singh *et al.* 2016). Some researchers have reduced the ash content and removed the hydrophobic waxy layer on the rice straw surface to improve the self-bonding properties, which is a key measure of suitability for reusing the rice straw. Kurokochi and Sato (2015) reduced the size by compressing the rice straw into a non-stick board after grinding the material into fiber particles. El-Kassas and Mourad (2013) used the rice straw to produce a straw-based medium density fiberboard in which the ash content was reduced *via* both physical and mechanical methods.

In this study, a low-concentration NaOH solution was used as a catalyst to pretreat the rice straw. The utilization performance of the rice straw was improved by removing lignin (Tsegaye *et al.* 2019) and effectively disrupting the structure of the rice straw (Dong *et al.* 2018) through a series of both chemical and physical reaction. This led to a modernized production process of small-sized rice straw block made by self-bonding under normal atmospheric temperature and pressure. The result of preliminary testing showed that the small-sized rice straw blocks demonstrated a better thermal performance, while the effect of improvement was closely related to the concentration of NaOH solution. When the concentration of NaOH solution was varied from 1% to 3%, the thermal resistance of the test block material ranged from 0.603 to 0.510 ($m^2 \cdot K$)/W (Tang *et al.* 2016), which represented a better thermal property than a common building blocks in Chongqing (a city in southwest China). This small-sized rice straw block pretreatment by low-concentration NaOH solution can be used as a kind of filling material for hollow building blocks.

## EXPERIMENTAL

### Materials and Methods

*Manufacture process of small-sized rice straw block*

Rice straw (XiDaYou216) was obtained from an experimental farm at Southwest University in Chongqing, located at 106.40°E, 29.80°N, in the southwest of China. The rice straw was stored in a room with a normal atmosphere temperature to confirm air-dryness. The whole stem of rice straw was selected, cleaned, and trimmed into small pieces (2 to 5 cm) with a grass cutter (Xianglong Hardware Machinery, Shandong, China).

The main preparation process of small-sized rice straw blocks is shown in Fig. 1. As the first step of the pretreatment to rice straw, the rice straw pieces were soaked in 10 times the straw weight of NaOH solution for a particular time. And through a rice straw softening pre-experiment with 1.5%, 4.5%, and 7.5% concentration of NaOH solution for 24 h, the best soften effect was observed when a 1.5% concentration of NaOH solution was applied. So the rice straw was pretreated with distilled water and 0.5%, 1%, 1.5%, 2%, 2.5%, 3% NaOH solution for 24 h, respectively for the further experiments. When the rice straw had been softened, the straw was placed into a wooden mold (13 cm × 13 cm × 19 cm), tamping it into a stable form with an automatic pressure tester.

The tester (SUNS, Shenzhen, China) applied vertical pressure at a loading speed of 0.1 $kN \cdot s^{-1}$, which can apply pressure up to 3 kN and hold for 10 to 30 s. After being cured for 28 days under ambient condition, after which the blocks had gained an apparent density of 213 to 231 kg·m$^{-3}$, the rice straw blocks were placed into hollow concrete blocks to produce a thermal insulation building material.

*Thermogravimetric ash analysis*

In order to evaluate the softening effect, the residual amount of ash was measured on the surface of the rice straw pretreated with distilled water and 0.5%, 1%, 1.5%, 2%, 2.5%, and 3% NaOH solution. The method was obtained from the National Pharmacopoeia Commission (2015), and it requires the use of the sample (2 to 3 g) in a crucible with a constant combustion quality. So 2 g of rice straw of each group was placed in a crucible and then slowly heated without burning the straw. With the heating process going on, the temperature in the crucible began to increase as soon as the sample had completely carbonized. After a constant temperature of 550 °C was applied for 3 h in the crucible, the sample was entirely ashed. After that, the ash content (%) in the sample could be calculated from the residual ash.

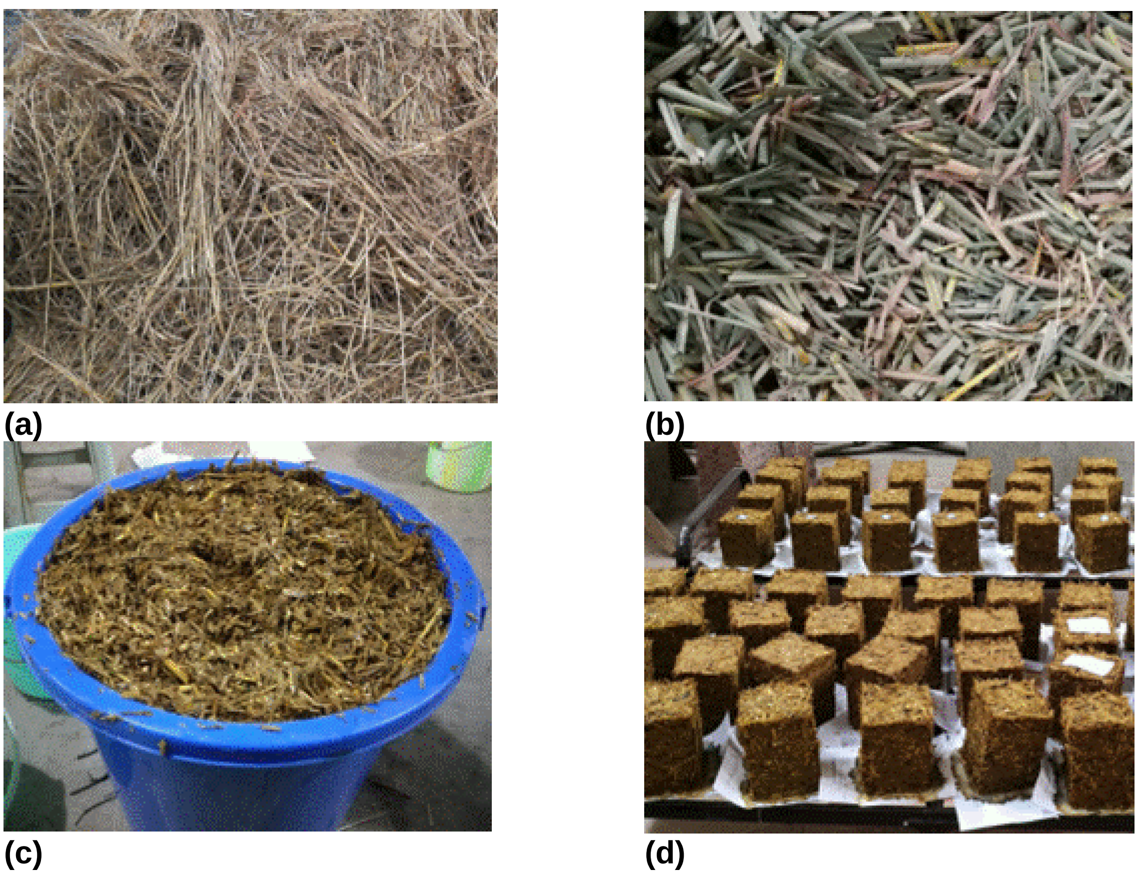



**Fig. 1.** Rice straw blocks molding process: (a) Rice straw was drying in the air; (b) Rice straw trimmed with a grass cutter; (c) Rice straw was pretreated with NaOH solution; (d) Rice straw was formed into small-sized blocks

*Scanning electron microscopy*

The morphological and elemental analyses were conducted with rice straw rods soaked in distilled water or 1% NaOH solution, using SEM (Phenom-World, Eindhoven, Netherlands) to provide scanning. Before the scanning, 300i nano gold was sprayed on the surface of the sample. Then conductive adhesive was used to fix the sample on the T-stage to enable acquisition of images.

## RESULTS AND DISCUSSION

### Thermogravimetric Ash Analysis

The residual ash content of each group after pretreatment is shown in Table 1. The Shabu-shak constant weight is the weight of each sample prepared in the crucibles with a constant combustion quality. The ash weight is the weight of the residual ash content after the thermogravimetric ash analysis, and the percentage shows the residual ash percentage of Shabu-shak constant weight in each group.

Through further analysis, structures attached to the rough rice straw rod surface mainly consist of $SiO_2$ (Inglesby *et al.* 2005) and a large quantity of $SiO_2$ was found in the residual ash from this study. The Percentage showed that the ash content of rice straw samples treated with NaOH solution was effectively decreased compared with samples treated with distilled water. Secondly, the content of ash varied from 8.71% to 12.45% when samples had been pretreated with 0.5% to 3% NaOH solution for 24 h. And thirdly, as the concentration of NaOH solution was raised progressively, the content of ash displayed a reduction at first and then it began to increase.

In summary, the most significant effect of the pretreatment of rice straw among the test procedure was observed when a 1% NaOH solution was adopted.

**Table 1.** Ash Content of Rice Straw Pretreated with Different Concentrations of NaOH Solution

| Project | NaOH Concentration (%) | Sample Weight (g) | Shabu-shak Constant Weight (g) | Ash Weight (g) | Percentage (%) |
|---|---|---|---|---|---|
| 1 | Distilled Water | 32.03 | 31.61 | 6.29 | 19.89 |
| 2 | 0.50 | 45.49 | 45.29 | 4.12 | 9.10 |
| 3 | 1.00 | 34.19 | 33.99 | 2.96 | 8.71 |
| 4 | 1.50 | 46.42 | 46.19 | 4.91 | 10.63 |
| 5 | 2.00 | 35.95 | 35.69 | 4.21 | 11.79 |
| 6 | 2.50 | 46.74 | 46.44 | 5.56 | 11.98 |
| 7 | 3.00 | 45.63 | 45.33 | 5.64 | 12.45 |

### Scanning Electron Microscopy Analysis

The apparent morphology of the rice straw through SEM scanning is shown in Fig. 2. There were three kinds of apparent structures on the surface of the rice straw, as observed through the SEM scope. These were categorized as a thorny structure (Fig. 2a), a spherical protuberance structure (Fig. 2b), and a rod-shaped particle structure (Fig. 2c). These structures were quantitated using Image-pro Plus 6.0 image-processing software, and the results are shown in Table 2.

The surface of the rice straw rod was uneven, attached to many thorny structures. These thorny structures were arranged very closely, and most of these consisted of impurity mixtures. The thorny structure was the largest among the three structures and it contained lots of morphological differences. It had a bottom diameter of 15.9 ± 5.0 μm, a length of 34.1 ± 4.3 μm and its distribution on the rice straw surface is looser than the other two structures.

The surface of the sample pretreated with NaOH became flatter but still some pits remained on the surface (Fig. 2b), which indicates that the NaOH pretreatment process had digested the apparent thorny structure of the rice straw.

The spherical protuberance structures distributed on the surface were much smaller than the thorny structures, and their size ranged from 2.5 μm to 3.3 μm, with a roundness of 4.6 ± 1.8 μm. Not like the other two structures, the arrangement of the spherical protuberance structure was more regular and closer (Fig. 2c). After the NaOH pretreatment process, the great majority of these protuberances were observed to have been dissolved (Fig. 2d).

With the scanning enlargement raised to 5000x, many rod-shaped particle structures distributed on the entire cell wall of rice straw became apparent (Fig. 2e). The rod-shaped particle structures were tiny, with a long tail of 0.62 ± 0.08 μm and a short tail of 0.071 ± 0.019 μm. These particles were attached to the bigger spherical protuberance structures (Fig. 2e). The NaOH solution dissolved the spherical protuberances, depriving the attachment of these to the rod-shaped particles and bringing them beyond the material's surface. In the meantime, some particles were also digested by NaOH, making the surface of the cell wall flatter and smoother (Fig. 2f).

The apparent structures have been described as being harmful to the rice straw's self-bonding ability (Kurokochi and Sato 2015), and the present work showed that NaOH solution could remove these structures efficiently. Moreover, the rice straw is coated by a waxy layer, which is hydrophobic (Li *et al.* 2010). The NaOH pretreatment process may dissolve the waxy layer, exposing the internal structure and enhancing the wettability of the rice straw (Zhang *et al.* 2015). As a result, the NaOH pretreatment process could tend to remove obstructions such as a waxy layer, thus increasing the accessibility of cellulose to the water at the outside surfaces.

Thus, a conclusion can be reached that after the destruction of the apparent structures and the solution of the waxy layer by NaOH, the water could play a role as a binder to enhance the "biting force" straw-to-straw, increasing the rice straw's water-holding capacity and making it easier to form the rice straw into a block. This explanation matches with Phuong's study (Phuong *et al.* 2017).

**Table 2.** Main Material and Distribution Statistics of Straw Rod Diameter

| Material | Average | SD | Average | SD | Density (pieces·mm$^{-2}$) |
|---|---|---|---|---|---|
| TS (Fig. 2a) | Bottom diameter (μm) | | Length (μm) | | 67.58 |
| | 15.8754 | 5.016 | 34.0908 | 4.2807 | |
| SP (Fig. 2c) | Diameter (μm) | | Roundness (μm) | | 5.25 × 10$^{4}$ |
| | 2.8866 | 0.4157 | 4.584 | 1.8272 | |
| RP (Fig. 2e) | Long trail (μm) | | A short trail (μm) | | Over the surface |
| | 0.6217 | 0.0811 | 0.0713 | 0.0188 | |

Note: TS, thorny structure; SP, spherical protuberance structure; RP, rod-shaped particle structure.

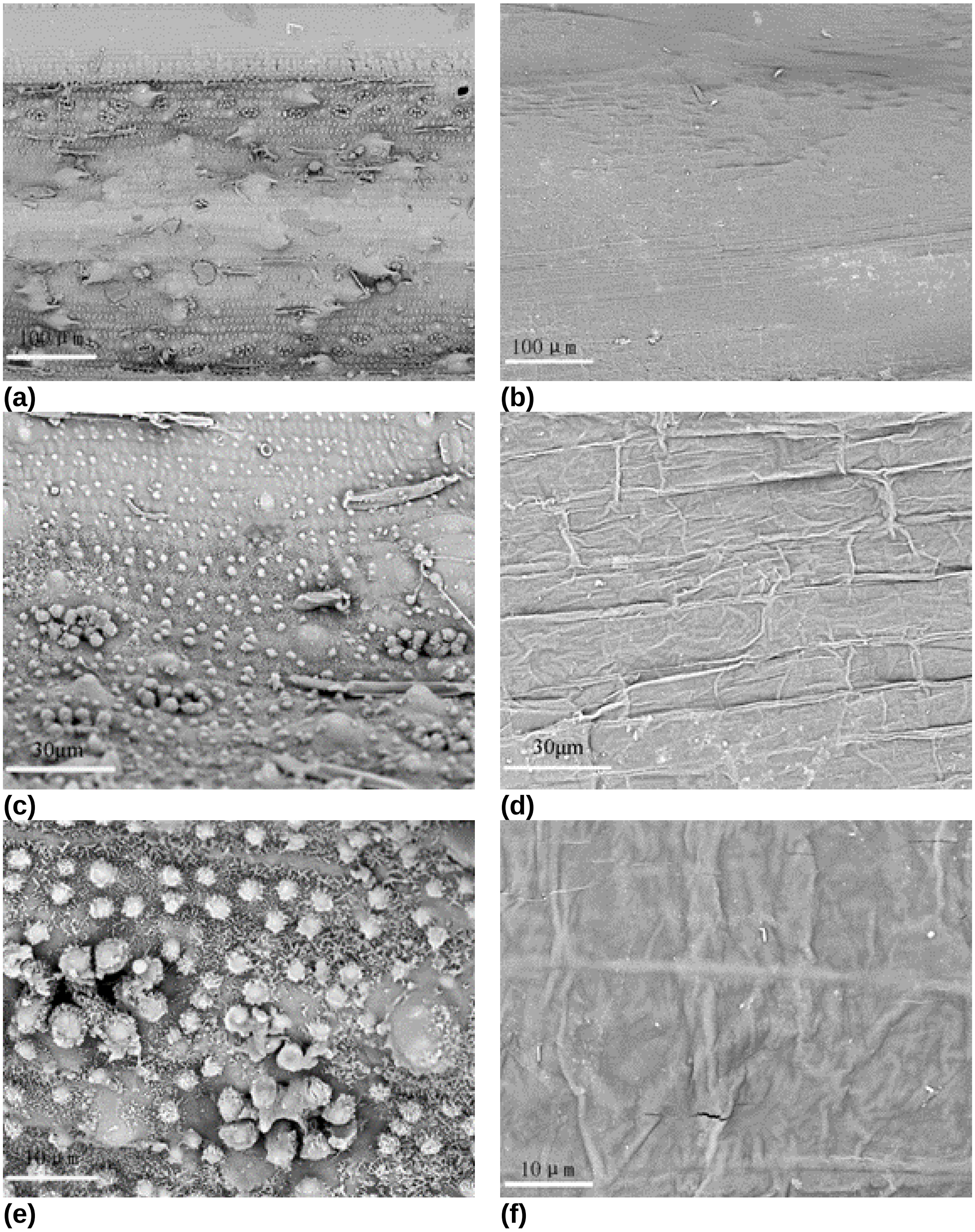



**Fig. 2.** Apparent morphology analysis of rice straw by SEM. Sample pretreated with distilled water magnified at (a) 500×, (c) 2000×, or (e) 5000×. Sample pretreated with NaOH magnified at (b) 500×, (d) 2000×, or (f) 5000×.

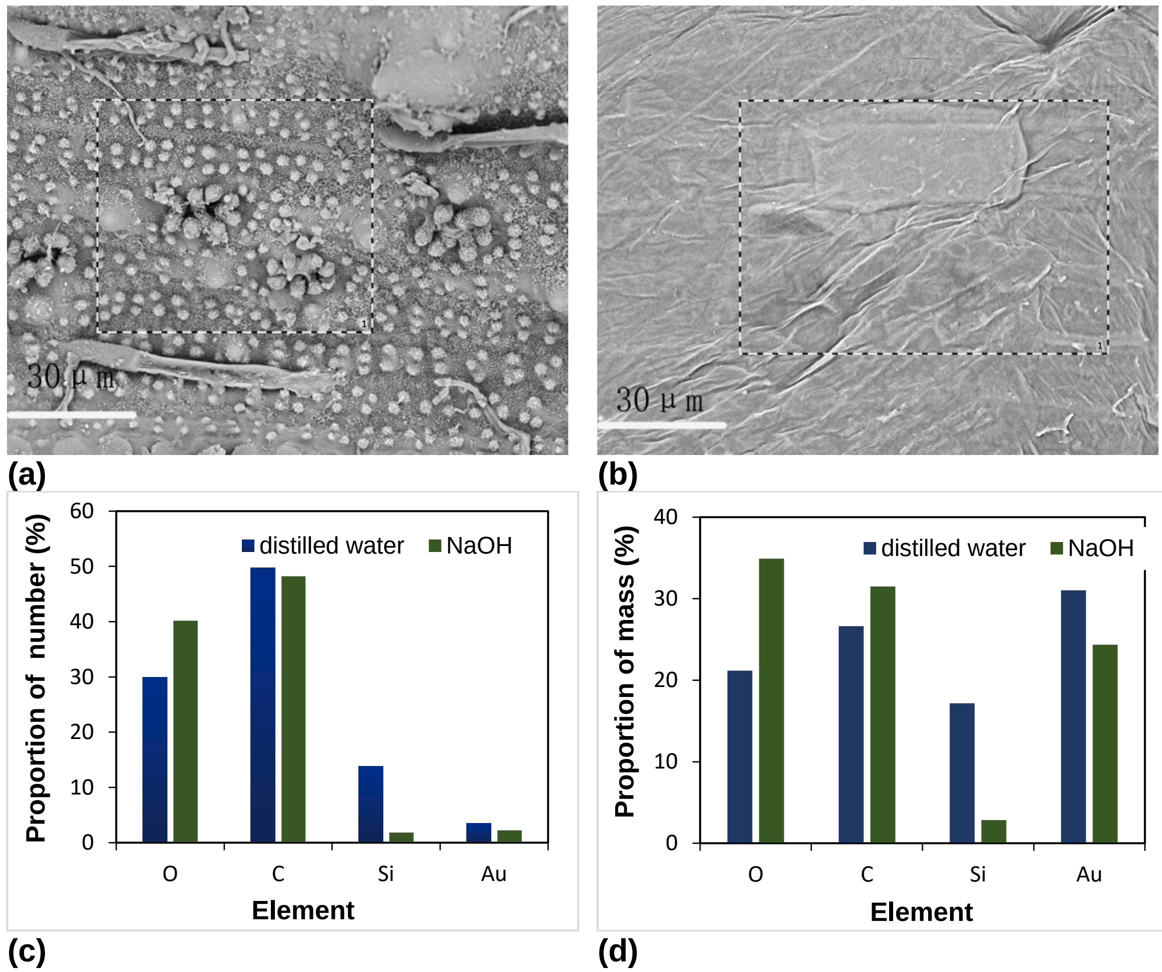



**Fig. 3.** The varieties of the appearance of the elemental test area and the major element. (a) Elemental test areas of sample pretreated with distilled water; (b) Elemental test areas of sample pretreated with NaOH solution; (c) The proportion of number on the surface of the sample; (d) The proportion of mass on the surface of the sample

## Elemental Analysis

The results of the elemental analysis on the sample's surface are shown in Fig. 3. After the pretreatment process, the proportion of the mass of oxygen and carbon, which belong to organic matter, slightly increased, and the content of silicon and gold, belong to inorganic matters, decreased. Actually, this result of the elemental testing was quite similar to that of the ash test.

In total, all of these elements in the rice straw decreased after the NaOH pretreatment process. But in comparison, the relative molecular masses of silicon or gold are heavier than oxygen or carbon, which makes the decreasing of the mass ratio more intense. As a result, the mass ratio of oxygen and carbon increased relatively. This explained why the proportion of the mass of oxygen and carbon rather increased after the NaOH pretreatment process in Fig. 3d. However, the mass of oxygen and carbon did show a loss in the rice straw. Because the organic matter such as waxy substances and lignin mainly consists of oxygen, carbon, and hydrogen, so that the loss of oxygen and carbon means that NaOH solution removed the waxy layer around the straw and digested the lignin parts in the rice straw, turning it into something soluble, cut off the organic viscous connection between the straw fiber surfaces. The most severe variation of the mass proportion was displayed in the case of silicon, which was decreased by 12.0%. The silicon mainly exists as $SiO_2$ in the rice straw, in which $SiO_2$ is insoluble in water and underlies the rigidity of the rice straw material (Inglesby *et al.* 2005). Besides, $SiO_2$ is an important part of the thorny structure, spherical protuberance structure, and rod-shaped particle structure. The loss of silicon represents that $SiO_2$, as well as the microstructure above attached to the rice straw surface, had been dissolved or turned into sodium silicate after the NaOH pretreatment process.

In summary, under the chemical reactions of lignin and $SiO_2$, the rigidity of rice straw decreased significantly, making the rice straw biomass material easier to process further as a result.

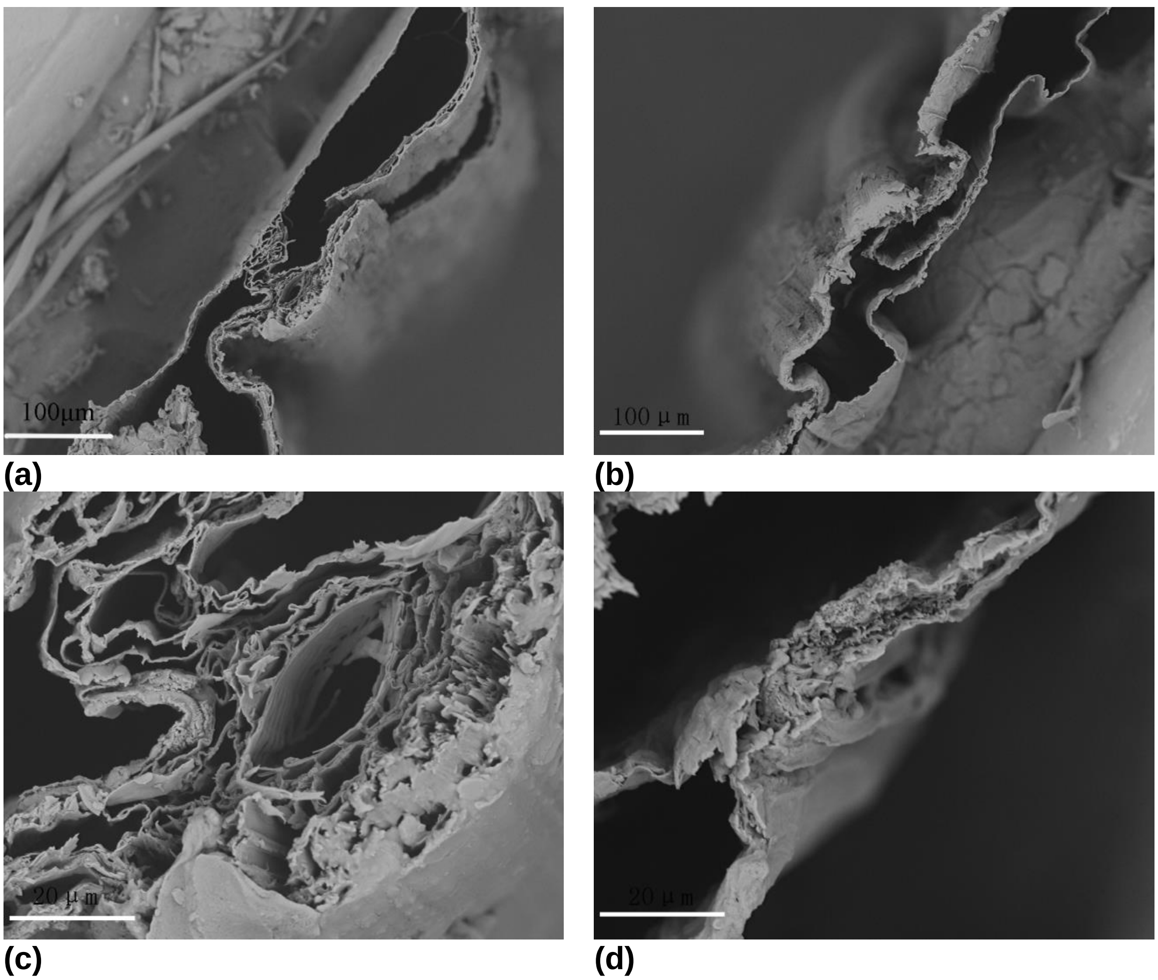


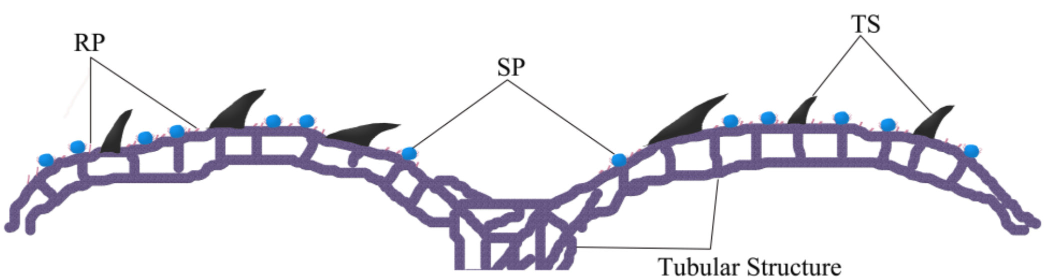

**Fig. 4.** Sectional microscopic morphology of rice straw. Sample pretreated with distilled water magnified at (a) 500× and (c) 3000× Sample pretreated with NaOH magnified at (b) 500× and (d) 3000×

## Specimen Section Analysis

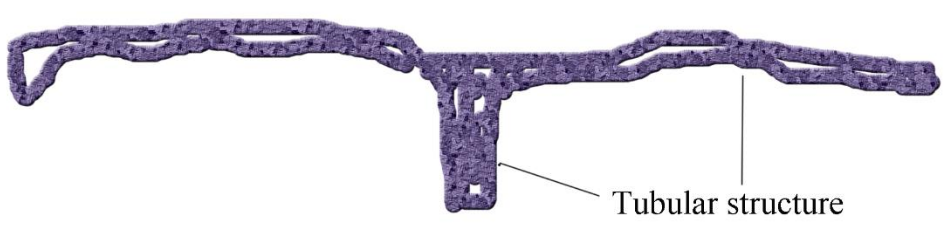
The results of specimen section analysis are shown in Fig. 4, in which the effect of the NaOH pretreatment process could describe in the recombination of the layered structures and the disruption of the “connecting belt”.

In Fig. 4a, the image shows that the rice straw rod consisted of a few layered structures. These structures were arranged in a quite dispersed manner, which leads to the formation of many hole-like structures, making the layered structures porous and loose. After the NaOH pretreatment process, the hole-like structures decreased a lot. In the meantime, the space between the multilayered structures was gradually reduced and the layered structures finally recombine into a single-layered, dense structure (Fig. 4b).

In Fig. 4c, the image shows the section structure of the rice straw rod and the internal "connecting belt" structure. The "connecting belt" offers a compact connection between tubular thick-walled cell structure and other substances, which protects and supports the stability of rice straw but provides a negative effect on the self-bonding ability as well as the adhesion effect between the rice straw pieces (Su *et al.* 2015). However, the "connecting belt" structure almost disrupt and turns into a flocculent structure after the NaOH pretreatment process (Fig. 4d), which proves a positive factor in the rice straw soften procedure.




**(a)**




**(b)**

**Fig. 5.** Model of untreated (a) and model of treated (b) rice straw

As shown in the cross-sectional model in Fig. 5, there was a distribution with a thorny structure, spherical protuberance structure, and rod-shaped particle structure on the surface of the rice straw tubular structure. These structures were hydrophobic, covered by a waxy layer, containing much silicon, provide stability of the rice straw (Raita *et al*. 2017). With the pretreatment of the NaOH solution, the internal tubular constrained structure and the hard-hydrophobic layer on the surface of the rice straw were digested (Fig. 5b). In addition to the combined action of the recombination of the layered structures and the disruption of the "connecting belt", the wettability of the rice straw was enhanced, and the rice straw was softened.

In conclusion, the pretreatment process of NaOH leads to two physical variations, which are the recombination of the layered structures and the disruption of the "connecting belt". The self-bonding property of rice straw improves significantly under both compactions of physical variations and chemical reactions.

## CONCLUSIONS

1. The pretreatment of rice straw in Chongqing with a 1% NaOH solution for 24 h led to the lowest ash content and the best softening effect.
2. There are many types of imperfections on the surface of the untreated rice straw. Thorny structure, spherical protuberance structure, and rod-shaped particle structure material are widely distributed, and these structures contain quite a large amount of silicon. These structures are hard and hydrophobic, which is an explanation of why rice straw could rarely self-bonding.
3. After pretreatment by NaOH, the apparent hydrophobic wax layer on the surface of rice straw was digested, and the original tubular structure of rice straw could not easily maintain stability. The rice straw became soft and easier to produce small-sized rice straw blocks.
4. However, the relationship between ash and rice straw in terms of self-adhesion needs to be further studied. A rod-like structure on the surface of the original rice straw was spread all over the surface. It is still unclear whether the apparent hydrophobicity of rice straw is related to the rod-like particle structure.

### Declarations of Conflict of Interest

None.

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