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Study on Improving Physical–Mechanical Properties and Frost Resistance of Straw–Mortar Composite Wall Materials by Pretreatment

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Abstract: In recent years, China has increased the material utilization of crop straw, and the strength of straw–mortar composite wall materials is low, which limits their large-scale utilization. Pretreatment can improve the physico-mechanical and frost resistance properties of straw–mortar composite wall materials. In this study, the Box–Behnken design in the Design-Expert software was used to design and carry out a three-factor and three-level interactive experiment and freeze–thaw cycle experiment with the straw content, pretreatment time, and reagent concentration as influencing factors, and the compressive strength, water absorption rate, and dry density as response values. The results showed that the impact of each factor on the response value, from high to low, was the straw content, pre-preparation time, and reagent concentration. When the straw content was 10%, the preparation time was 5 min, and the reagent concentration was 5%, the physical and mechanical properties of the straw–mortar composite wall material were the best. At the same time, the compressive strength was 6.52 MPa, the water absorption rate was 17.7%, and the dry density was 1396.33 kg·m^{-3}, which was 67% higher, 31% lower, and 37% higher than that of the untreated straw–mortar composite wall materials. After the freeze–thaw cycle, the mass loss rate of the composite materials was less than 5%, which met the requirements of the frost resistance specifications; the strength loss rate of the composite materials varied between 19.7% and 27.8%, although some test blocks did not meet the requirements of less than 25% in the specification. The compressive strength was greatly improved compared with the untreated composite materials in the related research, and the water absorption rate was about 25% lower than that of the untreated straw–mortar composite wall materials. Pretreatment significantly improved the physico-mechanical and frost resistance properties of the straw–mortar composite wall materials.

Keywords: straw materialization application; NaOH pretreatment; compressive strength; water absorption rate; dry density; freeze–thaw cycle

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1. Introduction

Crop straw resources are abundant in China, but their comprehensive utilization rate is relatively low, which has a great impact on the environment and human health [1]. Clay bricks widely used in rural areas have many problems, such as high energy consumption and the large utilization of land resources, which have put great pressure on China's energy resources and living environment protection [2]. It has been found that wall material prepared by combining straw with traditional building materials has the advantages of economy, energy saving, and environmental protection—this is an important form of the material utilization of straw [3]. However, the low strength of straw composite materials is not conducive to their large-scale application in building walls [4].

The poor compatibility between straw and Portland cement and the relatively high moisture content of straw fiber are important reasons for the poor physical and mechanical

properties of straw composites [5,6]. The chemical pretreatment of straw can remove most non-cellulosic substances and hydrophilic chemicals on the straw surface [7–11]. It increases the surface roughness of the fiber, enhances the combination of the fiber and matrix, improves the stress transfer mode between the materials [12,13], reduces the water absorption rate, improves the workability of the straw materials, and enhances the physical and mechanical properties of composite materials. With the increase in the solution concentration and pretreatment time, the strength of the straw composites increases [14]. Related studies show that the combined pretreatment has the advantages of being less time-consuming [15], having a better effect, and costing less than a single form of pretreatment. Zhang et al. [16] combined an acid treatment with hydrothermal carbonization, Chen et al. [17] combined an acid–alkali treatment with ball milling, Ma et al. [18] combined an alkali treatment with high-temperature steam blasting, and Akinyemi et al. [19] combined a sodium hydroxide reagent treatment and microwaves. All of these methods can significantly enhance the mechanical properties of composite materials.

The increase in straw content, as a plant aggregate, can lead to a decrease in the density and an increase in the porosity of composite materials, thus affecting the physical and mechanical properties of composite materials [20–22]. Feng et al. [23] and Wang et al. [24] concluded that, with the increase in straw content, the strength and dry density of the composite materials decreased and the water absorption rate increased. Huang et al. [25] found that, compared with untreated straw composite materials, the water absorption rate of alkali-treated composite materials decreased significantly.

In severely cold areas, the damage caused by the freeze–thaw cycle to building materials is very significant. The repeated freezing and thawing of a material will lead to the generation, expansion, and penetration of cracks, and then cause serious damage to the structure [26]. Hua et al. [27] found that the compression ratio was highly correlated with the residual strength of cement mortar after a freeze–thaw cycle. Rangel et al. [28] found that the compressive strength and quality of concrete mixtures decreased after 150 and 300 freeze–thaw cycles. Wu et al. [29] found that adding an appropriate amount of basalt fiber could improve the frost resistance of concrete.

It has been found that the chemical modification of straw can effectively improve surface chemical characteristics and adsorption properties [30]. At present, the common modification methods mainly include acid–base modification, grafting modification, and acid–base grafting modification.

The physico-mechanical and frost resistance properties of straw composite materials have difficulty meeting its materialized utilization. In this study, straw–mortar composite wall materials were prepared by the physical–chemical pretreatment of rice straw. Taking the straw dosage, pretreatment time, and reagent concentration as variables, the influence law of the compressive strength, water absorption, and dry density of the straw mortar composite wall material was studied. The regression equation was fitted to obtain the optimal value of each performance index and the influencing factor value. Finally, 5, 10, and 15 freeze–thaw cycles were carried out. The effect of pretreatment on improving the physical–mechanical and frost resistance properties of the composite materials was discussed, which provided a theoretical reference for the large-scale utilization of pretreatment straw composite materials.

2. Materials and Methods

2.1. Experimental Design

According to the Box–Behnken design, 17 groups of three-factor and three-level interactive experiments were carried out. Taking the straw content (x_1), pretreatment time, (x_2) and reagent concentration (x_3) as influencing factors, and the compressive strength (y_f), water absorption rate (y_w), and dry density (y_ρ) of the composite materials as response values, the effects of various influencing factors on the properties of straw–mortar composite wall materials were studied [31]. The main influencing factors and levels are shown in Table 1.

Table 1. Testing factors and levels of straw–mortar composite wall materials.

Factors	Levels		
	−1	**0**	**1**
x_1 (%)	10	14	18
x_2 (min)	5	15	25
x_3 (%)	1	3	5

2.2. Experimental Materials

2.2.1. Cement

The ordinary Portland cement was used in the test, and its basic property indices are shown in Table 2.

Table 2. Physical and mechanical properties of cement.

Specific Surface Area ($cm^2 \cdot g^{-1}$)	Density ($kg \cdot m^{-3}$)	Setting Time (Min)		Compressive Strength (MPa)	
		Initial Setting	**Final Setting**	**3 d**	**28 d**
3245	3150	183	237	25.4	49.5

2.2.2. Rice Straw

The mature rice straw was collected from the paddy field (123°33′50.49″ E, 41°49′7.44″ N) of Shenyang Agricultural University. The redundant roots and ears of rice straw were removed, and straw was crushed by a straw grinder (FS-100, Xingyang Chuangyou Machinery Equipment Co., Ltd., Xingyang, China), then stored in moisture-proof bags.

2.2.3. Aggregate

The fine aggregate used in the test was the natural river sand from Hun River in Liaoning Province.

2.2.4. Water

The water used for the test was ordinary tap water from the laboratory, with a pH value of about 7.

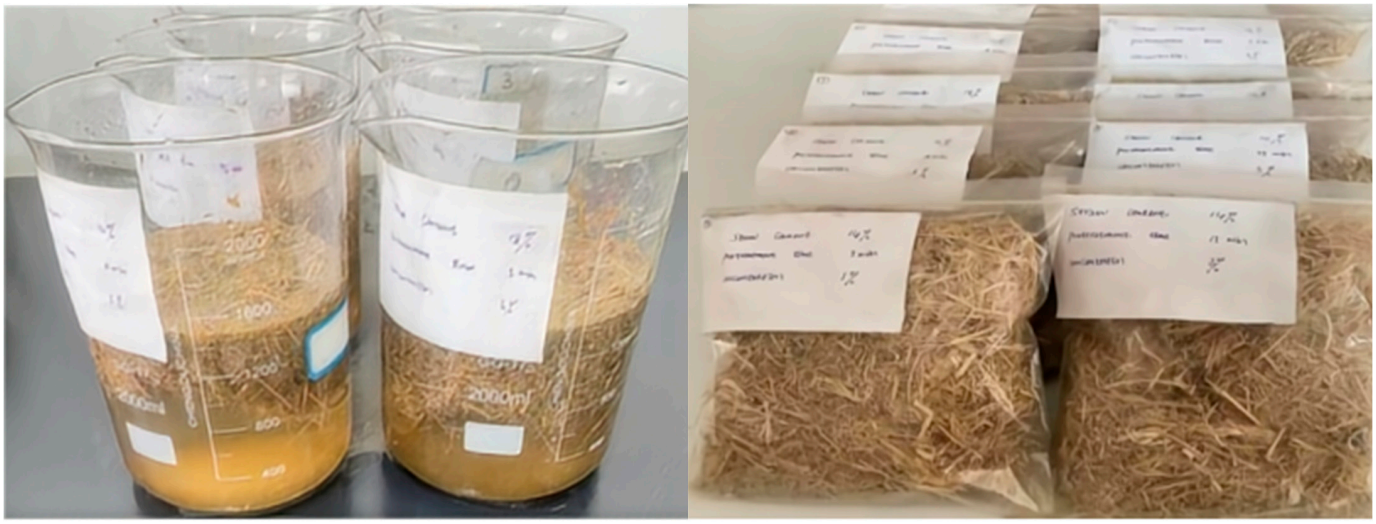
2.2.5. NaOH Reagent

The pretreatment NaOH reagent used in the test was Macklin sodium hydroxide reagent (S835850-500g, Shanghai Chemical Industry Park, Shanghai, China), which was a white solid particle with a component content not less than 99.5%.

2.3. Experimental Methods

2.3.1. Pretreatment

After selecting mature rice to remove straw, clean the surface dust, dry the ventilated place of the ceramic tile place, and crush with the plant grinder. The straw is soaked in the concentration of 5% sodium hydroxide solution, and stirred. The pretreatment time is 5, 15, and 25 min. Fish out the straw after processing, and dry with a dryer for reserve. The crushed straw was soaked in NaOH solution at room temperature at a solid–liquid ratio of 1:15 according to the set time and mass fraction [32]. After pretreatment, the straw was fished out and washed to neutral, then dried and put into moisture-proof bags [33], as shown in Figure 1.



(**a**) Samples during pretreatment. (**b**) Pretreated samples.

Figure 1. Combined pretreatment.

2.3.2. Determination of Compressive Strength

The mix ratio of straw mortar composite block is as follows: cement-and-sand ratio is fixed value m(cement):m(sand) = 1:3, straw content 10%, water–cement ratio 0.85, and water consumption 408.92 kg·m^{-3}. The compressive strength of composite materials was measured according to "Standard for Test Method of Basic Properties of Construction Mortar" [34], and the block size was 70.7 × 70.7 × 70.7 mm^3, as shown in Figures 2 and 3.



Figure 2. Testing block preparation.

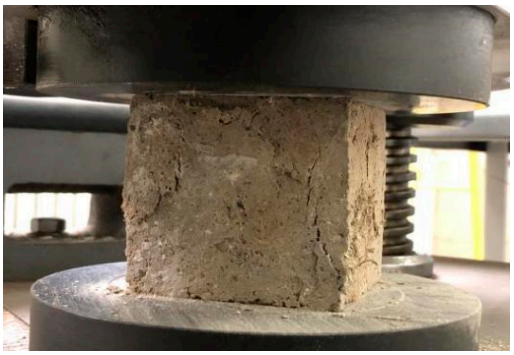


Figure 3. Determination of compressive strength.

2.3.3. Determination of Physical Property

(1) Water absorption rate

The test block was preserved for 28 days, immersed in water for 2 days, and then taken out. An electronic balance was used to weigh it. The water absorption rate was calculated according to Formula (1):

$$y_w = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where y_w is the water absorption rate of material, %; m_1 is the mass of specimen after water absorption, g; and m_0 is the mass of dried specimen, g.

(2) Dry density

After curing for 28 days, the test block was placed in the air-blast drying oven, and the dry density was determined according to "Dry–Mixed Thermal Insulating Mortar for Buildings" [35]. The dry density was calculated according to Formula (2):

$$y_\rho = \frac{m_0}{v} \quad (2)$$

where y_ρ is the dry density of composite materials, kg·m^{-3}; m_0 is the constant mass of composite materials after drying, g; and v is the volume of composite materials, cm^3.

2.3.4. Determination of Frost Resistance

The frost resistance of straw–mortar composite wall materials was studied by water freezing and water melting method. The test referred to the method of "Standard for Test Method of Performance on Building Mortar" (JGJ/T70-2009). The freeze–thaw devices used in this test are shown in Figures 4 and 5.



Figure 4. Testing device of freeze–thaw cycles.



Figure 5. Controller.

Mass Loss Rate

The mass loss rate of specimens after freeze–thaw cycles was calculated according to Formula (3):

$$\Delta m = \frac{m_1 - m_2}{m_1} \times 100\% \quad (3)$$

where Δm is mass loss rate of specimens after freeze–thaw cycles, %; m_1 is constant mass of specimens after drying without freeze–thaw cycles, g; and m_2 is drying mass of specimens after freeze–thaw cycles, g.

Strength Loss Rate

The strength loss rate of specimens after freeze–thaw cycles was calculated according to Formula (4):

$$\Delta y_f = \frac{y_{f_1} - y_{f_2}}{y_{f_1}} \times 100\% \quad (4)$$

where Δy_f is compressive strength loss rate of specimens after freeze–thaw cycles, %; y_{f_1} is compressive strength of specimens without freeze–thaw cycles, MPa; and y_{f_2} is compressive strength of specimens after freeze–thaw cycles, MPa.

3. Test Results and Analysis of Physical and Mechanical Property Index of Straw–Mortar Composite Materials

The compressive strength (y_f), water absorption rate (y_w), and dry density (y_ρ) of the test blocks were measured, and the results are shown in Table 3. The ranges of the compressive strength, water absorption rate, and dry density were 2.2~7.3 MPa, 11.8~29.4%, and 1020.06~1672.10 kg·m^{-3}, respectively. The experimental results of groups 3, 5, 6, 7, 10, and 12 showed that the increase in straw content was inversely proportional to the compressive strength and dry density, and directly proportional to the water absorption rate. The increase in reagent concentration was positively correlated with the compressive strength and dry density, and negatively correlated with the water absorption rate. The increase in pretreatment time was positively correlated with the compressive strength and dry density, and negatively correlated with the water absorption rate.

Table 3. Physical and mechanical properties of composite materials based on the Box–Behnken experimental design.

Number	x_1 (%)	x_2 (Min)	x_3 (%)	y_f (MPa)	y_w (%)	y_ρ (kg·m^{-3})
0	10	15	3	3.88	13.5	1020.06
1	14	15	3	5.06	24.9	1478.93
2	14	15	3	5.01	13.7	1651.73
3	14	5	1	4.40	24.9	1307.64
4	14	15	3	5.11	29.4	1318.58
5	10	25	3	6.50	11.8	1672.10
6	14	5	5	4.80	23.6	1278.78
7	18	15	1	2.20	24.8	1295.76
8	10	15	5	7.30	16.3	1569.10
9	14	15	3	5.08	24.1	1358.57
10	14	25	1	4.02	22.7	1359.71
11	14	25	5	5.50	21.9	1369.33
12	10	5	3	6.10	20.2	1402.72
13	18	5	3	2.50	21.8	1432.72
14	18	15	5	3.20	24.4	1315.56
15	18	25	3	2.90	28.9	1195.02
16	10	15	1	5.60	17.1	1466.67
17	14	15	3	5.04	20.2	1465.53

where x_1 is the straw content (%, mass fraction); x_2 is the pretreatment time (min); x_3 is the reagent concentration (%, mass fraction); y_f is the compressive strength (MPa); y_w is the water absorption rate (%, mass fraction); and y_ρ is the dry density (kg·m^{-3}).

3.1. Modeling and Analysis of Variance (ANOVA)

By fitting the physical and mechanical property indices in Table 3, a quadratic polynomial regression equation with compressive strength y_f, water absorption rate y_w, and dry density y_ρ as response values and three factors as independent variables was obtained, as shown in Formula (5), (6), and (7), respectively.

$$y_f = 4.2236 + 0.1881x_1 + 0.0418x_2 + 0.6188x_3 - 0.0219x_1x_3 + 0.0135x_2x_3 - 0.0208x_1^2 - 0.002x_2^2 \quad \left(R^2 = 0.9958\right) \quad (5)$$

$$y_\omega = -9.5049 + 3.5981x_1 + 3.4363x_3 + 0.0086x_1x_2 - 0.1023x_1^2 - 0.6469x_3^2 \quad \left(R^2 = 0.9261\right) \quad (6)$$

$$y_\rho = 1664.7529 - 8.2502x_1 - 1.1776x_1x_2 - 2.5822x_1x_3 + 0.2192x_1^2 - 0.794x_2^2 \quad \left(R^2 = 0.8342\right) \quad (7)$$

where x_1 is the straw content of the composite material, % (mass fraction); x_2 is the pretreatment time of straw, min; x_3 is the reagent concentration, % (mass fraction); y_f is the compressive strength of the composite material, MPa; y_w is the water absorption rate of the composite material, % (mass fraction); and y_ρ is the dry density of the composite material, $kg \cdot m^{-3}$.

R^2 indicates the extent to which the constructed response surface model reflects the evolution of the results. The closer its value is to 1, the better the model fitting degree is.

The response values of the physical and mechanical properties of each group were analyzed by a variance analysis and significance test, and the results are shown in Table 4.

Table 4. Coefficient values and variance analysis of the fitted model for different responses of composite materials.

Response Variable	Source	Sum of Squares	*df*	Mean Squares	F Value	*p* Value	Significance
Compressive strength	Model	31.07	9	3.45	186.01	<0.0001	**
	x_1	27.01	1	27.01	1455.57	<0.0001	**
	x_2	0.16	1	0.16	8.45	0.0228	*
	x_3	2.62	1	2.62	141.30	<0.0001	**
	x_1x_3	0.12	1	0.12	6.60	0.0370	*
	x_2x_3	0.29	1	0.29	15.71	0.0054	**
	x_1^2	0.47	1	0.47	25.08	0.0016	**
	x_2^2	0.22	1	0.22	11.74	0.0110	*
	Lack of fit	0.12	3	0.041	28.53	0.0037	
Water absorption rate	Model	148.47	9	16.50	9.75	0.0033	**
	x_1	102.46	1	102.46	60.56	0.0001	**
	x_3	1.32	1	1.32	0.78	0.0463	*
	x_1x_2	0.47	1	0.47	0.28	0.0447	*
	x_1^2	11.29	1	11.29	6.67	0.0363	*
	x_3^2	28.19	1	28.19	16.66	0.0047	**
	Lack of fit	10.49	3	3.50	10.31	0.0236	
Dry density	Model	1.413×10^5	9	15,705.00	3.91	0.0429	*
	x_1	96,965.07	1	96,965.07	24.16	0.0017	**
	x_1x_2	64,280.00	1	64,280.00	6.30	0.0404	*
	x_1x_3	1706.93	1	1706.93	0.17	0.0447	*
	x_1^2	3055.51	1	3055.51	0.30	0.0312	*
	x_2^2	26,544.84	1	26,544.84	6.61	0.0369	*
	Lack of fit	3921.89	3	1307.30	0.22	0.8805	

where x_1 is the straw content (%, mass fraction); x_2 is the pretreatment time (min); x_3 is the reagent concentration (%, mass fraction); "*" means generally significant difference at $p < 0.05$ level; and "**" means extremely significant difference at $p < 0.01$ level.

From the results in Table 4, it could be seen that the straw content had an extremely significant influence on all response variables. The reagent concentration had an extremely significant effect on the compressive strength and a significant effect on the water absorption rate. The pretreatment time had a significant influence on the compressive strength. The

interaction between the straw content and reagent concentration had a significant influence on the compressive strength and dry density. The interaction between the pretreatment time and reagent concentration had an extremely significant effect on the compressive strength. The interaction between the straw content and pretreatment time had a significant influence on the water absorption rate and dry density.

3.2. Influence of Interaction of Various Factors on Physical and Mechanical Properties

3.2.1. Influence of Interaction of Various Influencing Factors on Compressive Strength

By observing the response surface diagram, the influence level and regularity of the interaction of various factors on the response value can be significantly analyzed [36]. It could be seen from Figure 6 that, with the increase in reagent concentration, the compressive strength of the straw–mortar composite wall materials increased at a higher rate when the straw content was low and the pretreatment time was long. When the straw content was high and the pretreatment time was short, the compressive strength of the straw–mortar composite wall materials increased slowly. With the increase in straw content, the reduction rate of the compressive strength of straw–mortar composite wall materials with a low reagent concentration was smaller than that with a high reagent concentration. With the increase in pretreatment time, the compressive strength of the straw–mortar composite wall materials increased first, and then decreased with a small change rate when the concentration of the reagent was low. When the reagent concentration was high, the compressive strength of the straw–mortar composite wall materials increased slowly.

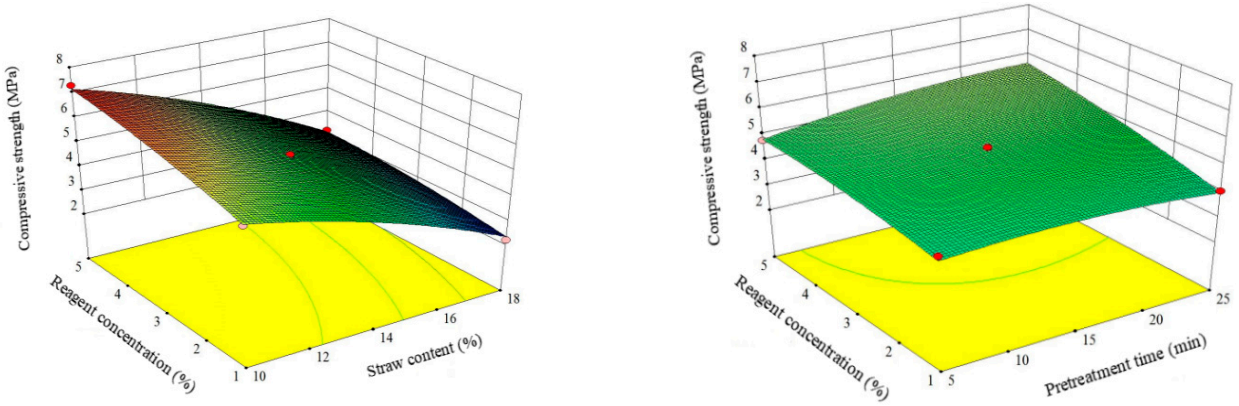


Figure 6. Response surface diagram of interaction of various factors on the compressive strength.

The increase in straw content was the main reason for the rapid reduction in compressive strength. As straw fiber replaced part of the cement in cement mortar, the cement dosage decreased and mortar porosity increased; moreover, after the straw was mixed with cement, the hydration reaction between the straw and cement occurred, and the dissolved matter released by the eroded straw was converted into sugar acid, forming a calcium sugar acid shell on the surface of the cement particles, which had a certain retarding effect on cement mortar [37]. However, the properties of the materials depended on the interface between the fiber and the matrix to a certain extent [38]. Compared with the untreated straw, the surface roughness and fiber crystallinity of the straw fiber soaked in an alkaline solution were improved, which could better combine with the cement matrix, enhance the interface compatibility, and reduce the stress concentration, and effectively increase the strength of the composite materials [39,40]. In addition, pretreatment could promote the hydration reaction of cement [41], accelerate the generation of early calcium (hydrated calcium silicate) and ettringite, shorten the setting time, and, thus, improve the early strength of the materials.

3.2.2. Influence of Interaction of Various Influencing Factors on Water Absorption Rate

It could be seen from Figure 7 that, with the increase in pretreatment time, the water absorption rate of the straw–mortar composite wall materials decreased when the straw content was at a low level, and the decrease rate was relatively slow. When the straw content was at a high level, it increased. With the increase in straw content, the water absorption rate of the straw–mortar composite wall materials increased first, and then decreased when the pretreatment time was short, and increased significantly when the pretreatment time was long.

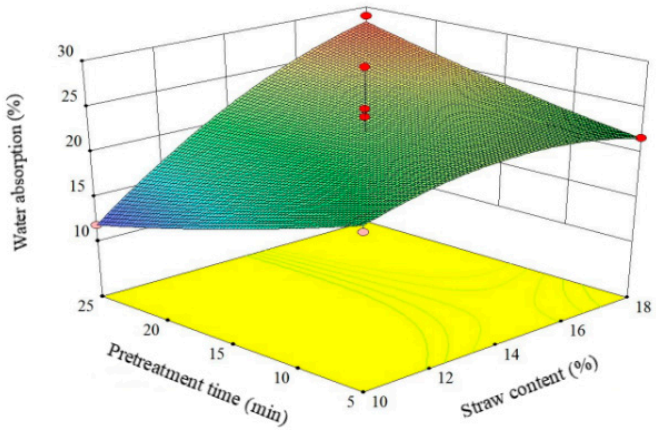


Figure 7. Response surface diagram of interaction between straw content and pretreatment time on the water absorption rate.

Straw was a hydrophilic porous material, and the straw–mortar composite wall material was a porous material. Increasing the content of straw would lead to an increase in the internal porosity of the material, so that the water absorption rate of the material would be improved [4]. However, a high water absorption rate would lead to micro-cracks in the composite materials, affecting the property of the composite materials [42]. Pretreatment could degrade the cellulose and hemicellulose in straw [43], and generate an esterification layer on the surface of the straw, which would increase the cohesion of the straw surface [44], reduce the internal porosity of the material, and significantly reduce the water absorption rate of the modified composite material. Jiang et al. [45] found that increasing the pretreatment time could increase the friction properties of the fiber surface, which was conducive to the glass fiber and high-density polyethylene by isopolymerization, thus reducing the water absorption rate of composites.

3.2.3. Influence of Interaction of Various Influencing Factors on Dry Density

It could be seen from Figure 8 that, with the increase in straw content, the dry density of the straw–mortar composite wall materials increased when the pretreatment time was short and decreased significantly when the pretreatment time was long and the reagent concentration was high, and the decrease rate was slow when the reagent concentration was low. With the increase in pretreatment time, the dry density of the straw–mortar composite wall materials increased significantly when the straw content was low, and decreased slowly first, and then rapidly when the straw content was high. With the increase in reagent concentration, the dry density of the straw–mortar composite wall materials increased slowly when the straw content was low, and increased first and then decreased when the straw content was high.

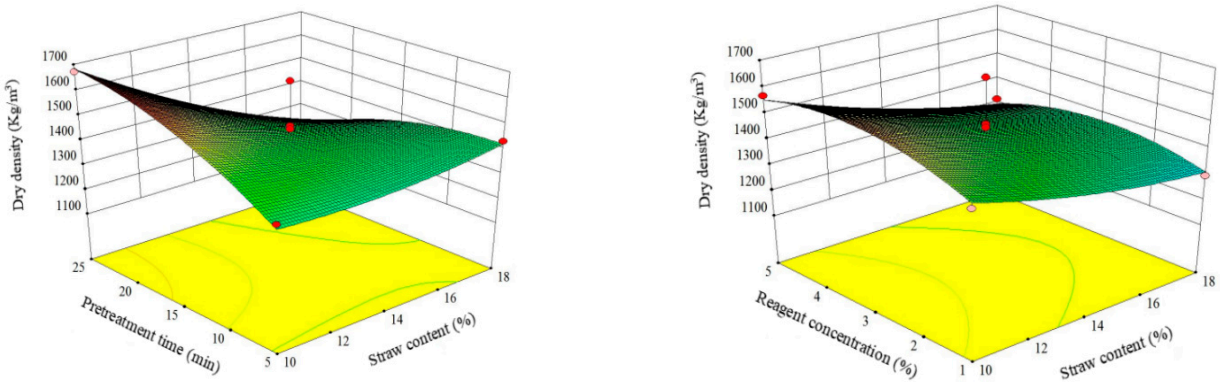


Figure 8. Response surface diagram of interaction of various factors on the dry density.

The density of straw was smaller than cement, so the dry density of the block can be obviously reduced by adding straw [46]. With the increase in straw content, the decrease extent of the dry density increased. However, after modification, part of the chemical components of the modified straw were decomposed, and it could be more evenly distributed in the mortar matrix without piling up [47]. Moreover, the combination of the fiber surface structure and the mortar matrix was more compact, so the dry density of the composite materials was higher than that of the unmodified composite materials. With the increase in straw content, the density of the composite materials decreased, but the density of the composite materials made of straw fiber after alkali treatment was higher than that of the untreated straw composite materials [48]. Under the condition of the same straw content, compared with unmodified straw, the sugar substance on the surface of the modified straw fiber had been removed, and, within a reasonable pretreatment time, with the increase in pretreatment time, the removal degree of the substance on the surface of the straw was higher, and the bonding conditions for the contact interface between the straw and mortar were better, so that the straw was more tightly bonded inside the mortar.

3.3. Parameter Optimization and Experimental Verification

Parameter optimization referred to the optimization design with the compressive strength, water absorption rate, and dry density as the target parameters within the horizontal range of three factors. The Design-Expert software 12.0 was used for analysis, and the set constraint conditions are shown in Table 5.

Table 5. Optimization goal of variables during straw–mortar composite wall materials production.

Variable	Goal	Level of Importance
Independent		
Straw content (%, mass fraction)	In range (10–18)	
Pretreatment time (min)	In range (5–25)	
Reagent concentration (%, mass fraction)	In range (1–5)	
Response		
Compressive strength (MPa)	Maximize	First
Water absorption rate (%, mass fraction)	Minimize	Second
Dry density (kg·m^{-3})	Maximize	Third

According to the "The Bricks & Blocks Composited Insulation Materials" [49], the strength of the wall block is not less than 3.5 MPa. Therefore, the compressive strength obtained by optimizing the parameters was 6.52 MPa, which showed that the compressive strength of the straw–mortar composite wall materials prepared in this experiment met the masonry requirements. The test results are shown in Table 6.

Table 6. Optimum conditions for producing straw–mortar composite wall materials.

x_1 (%)	x_2 (Min)	x_3 (%)	y_f (MPa)	y_ω (%)	y_ρ (kg·m^{-3})
10	5	5	6.52	17.7	1396.33

where x_1 is the straw content (%, mass fraction); x_2 is the pretreatment time (min); x_3 is the reagent concentration (%, mass fraction); y_f is the compressive strength (MPa); y_w is the water absorption rate (%, mass fraction); and y_ρ is the dry density (kg·m^{-3}).

The optimal conditions after optimization were tested and verified. The test results are shown in Table 7. It was verified that the measured value was close to the predicted value, which proved the accuracy of the optimized design. The experimental results showed that pretreatment could significantly improve the physical and mechanical properties of the straw–mortar composite wall materials. Devnani et al. [48] obtained that the mechanical strength of straw fibers treated with 5% alkali was significantly improved compared with untreated straw. Shang et al. [41] concluded that alkali treatment reduced the water absorption rate of straw fiber composites compared with untreated straw. Vijay et al. [50] found that alkali treatment could reduce the average diameter of the fiber by 21%, and increase the fiber density by 14.1%, because the voids and pores on the surface of the fiber were filled. These conclusions are consistent with the results of this study.

Table 7. Verification of experimental results.

x_1 (%)	x_2 (Min)	x_3 (%)	y_f (MPa)	y_ω (%)	y_ρ (kg·m^{-3})
10	5	5	6.49	17.8	1397.5

where x_1 is the straw content (%, mass fraction); x_2 is the pretreatment time (min); x_3 is the reagent concentration (%, mass fraction); y_f is the compressive strength (MPa); y_w is the water absorption rate (%, mass fraction); and y_ρ is the dry density (kg·m^{-3}).

4. Frost Resistance of Straw–Mortar Composite Wall Materials Produced with Treated Straw

In winter, straw–mortar composite wall materials will be eroded by rain and snow and damaged by freezing and thawing, so it is important to test its frost resistance. In this experiment, according to "Standard for Test Method of Performance on Building Mortar" (JGJ/T70-2009), the water freezing and water thawing method was selected to test the materials.

4.1. Influence of Freeze–Thaw Cycle on Mass Loss Rate

We measured the mass loss rate of the test blocks after 5, 10, and 15 freeze–thaw cycles, and the results are shown in Figure 9.

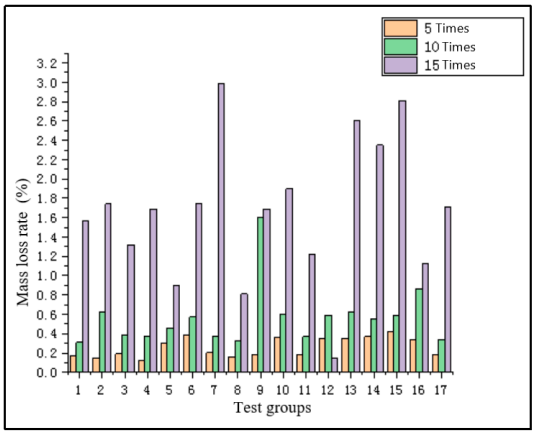


Figure 9. Mass loss rate of testing blocks after different number of freeze–thaw cycles.

It could be seen from Figure 9 that, with the increase in freeze–thaw cycles, the mass loss rate of 17 groups of straw–mortar composite wall material test blocks showed an increasing trend. Among them, after 5 freeze–thaw cycles, the change range of the mass loss rate of the test blocks was about 0.12~0.42%. After 10 freeze–thaw cycles, the mass loss rate varied from 0.31% to 0.86%. After 15 freeze–thaw cycles, the mass loss rate varied from 0.81% to 2.99%. According to "Building Thermal Insulation Mortar" (GB/T20473-2021), when the mass loss rate is within 5%, the material meets the frost resistance requirements. In this experiment, the mass loss rate under different freeze–thaw cycles were less than 5%, indicating that the material had good frost resistance.

4.2. Influence of Freeze–Thaw Cycle on Strength Loss Rate

We measured the strength loss rate of the test blocks after 5, 10, and 15 freeze–thaw cycles, and the results are shown in Figure 10.

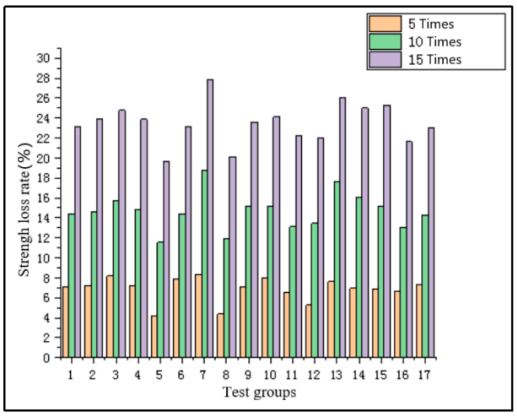


Figure 10. Strength loss rate of testing blocks after different number of freeze–thaw cycles.

It could be seen from Figure 10 that, with the increase in freeze–thaw cycles, the strength loss rate of 17 groups of straw mortar composite wall blocks showed an increasing trend. Among them, after 5 freeze–thaw cycles, the change range of the strength loss rate of the test block was about 4.2~8.3%. After 10 freeze–thaw cycles, the strength loss rate was about 11.5~18.8%. After 15 freeze–thaw cycles, the strength loss rate was about 19.7~27.8%. According to the specification requirements of "Building Thermal Insulation Mortar" (GB/T20473-2021), the strength loss rate can meet the frost resistance requirements within 25%. In this experiment, the strength loss rate under 5 and 10 freeze–thaw cycles were less than 25%, which indicated that the frost resistance was good. Although the strength loss rate of some test blocks exceeded 25% after 15 freeze–thaw cycles, compared with the strength loss rate of the untreated straw–mortar composite wall materials which was 34.0% after 15 freeze–thaw cycles studied by Yi [51], the compressive strength of the material in this test was greatly improved, up to 3.87 Mpa, and met the strength grade of masonry mortar MU3.5/A2.5. This was because the straw after the physical–chemical combined pretreatment was fibrous, which removed most of the non-cellulose materials on the surface and increased the roughness of the fiber surface [10,11]; the interfacial compatibility of mortar was better than that of segmental straw. After the freeze–thaw cycles, there were cavities in the position of the segmentary straw distribution in the unpretreated composite material, and some water existed in the cavities. When the materials froze, the water froze and expanded; when the expansion stress of the ice exceeded the cement stress of the mortar itself, tiny cracks would occur in the mortar; and, when the materials melted, the ice melted into liquid water and flowed into tiny cracks. After repeated freeze–thaw cycles, the strength of the material was greatly reduced [52]. The physical–chemical combined pretreatment could alleviate the uneven water content in the matrix, thus reducing the influence of the freezing–thawing cycle on cracks in the matrix, so the material had good frost resistance.

4.3. Influence of Freeze–Thaw Cycle on Water Absorption Rate

We measured the water absorption rate of the straw–mortar composite wall materials after 15 freeze–thaw cycles, and obtained the change in water absorption rate of the material at room temperature and after 15 freeze–thaw cycles, as shown in Figure 11.

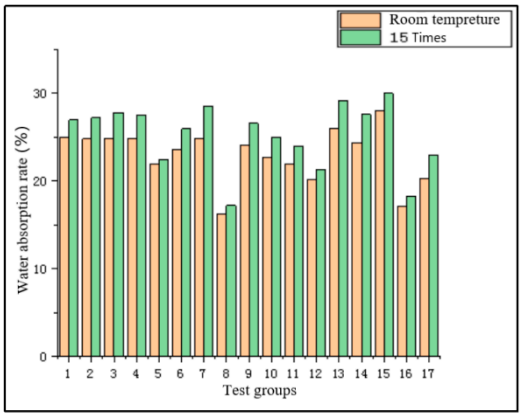


Figure 11. Water absorption rate of composite materials at room temperature after 15 freeze–thaw cycles.

It could be seen from Figure 11 that the water absorption rate of the material after the freeze–thaw cycle showed an overall upward trend. After 15 freeze–thaw cycles, the water absorption rate of the material ranged from 17.2% to 30.0%, and the water absorption rate of each group was less than 30%, and the water absorption rate after 15 freeze–thaw cycles increased by about 5.5% to 7.2% compared with that at room temperature.

5. Conclusions

Through a response surface methodology analysis, it was gleaned that the influence of the straw content on the compressive strength, dry density, and water absorption rate of straw–mortar composite wall materials was the most significant. The optimum factor level of the composite materials optimized by the Design-Expert software was a straw content of 10%, pretreatment time of 5 min, and reagent concentration of 5%. At the same time, the compressive strength of the material was 6.52 MPa, the water absorption rate was 17.7%, and the dry density was 1396.33 $kg \cdot m^{-3}$, which were 67% higher, 31% lower, and 37% higher than those of the untreated straw–mortar composite materials, respectively. The optimum physical and mechanical property parameters and pretreatment conditions provided a theoretical basis for the research and application of straw–mortar composites, and had a positive significance in promoting its large-scale utilization.

After 15 freeze–thaw cycles, the mass loss rate and strength loss rate of the materials showed an increasing trend, and the mass loss rate met the requirement of less than 5% in the standard. The compressive strength was 3.87 MPa, which was greatly improved compared with the untreated composite materials.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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