

Comparative Effects of Pretreatment on Composition and Structure of Corn Stalk for Biocomposites

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The outer surface of corn stalk (CS) plays a key role in the interfacial compatibility of non-wood-based panel products. To improve the bonding performance of the stalk surface, changes to the outer surface before and after four pretreatments (oxalic acid, oxalic acid + ultrasound, NaOH, NaOH + ultrasound) were investigated. Changes in the chemical composition, surface elements, aggregation structure, and microstructure of CS before and after pretreatment were analyzed. The results revealed that the wax layer, benzene–alcohol extract, and ash content of the outer surface of CS were decreased under different pretreatment conditions. The degree of reduction decreased in the order of NaOH + ultrasound > oxalic acid + ultrasound > NaOH > oxalic acid. The crystallinity of CS was obvious after pretreatment, and it increased in the order of oxalic acid + ultrasound > oxalic acid > NaOH + ultrasound > NaOH. Considering the properties of CS after pretreatment and the lignin activation modification of the CS surface, the optimal pretreatment conditions of CS were determined as oxalic acid + ultrasound, *i.e.*, 5% oxalic acid and ultrasonication at 50 °C for 1 h.

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Keywords: Corn stalk; Pretreatment; Oxalic acid; Crystallinity; Surface element; Microstructure

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INTRODUCTION

Crop straws are the fourth largest source of energy, with an annual production averaging 2.9 billion tons worldwide, led by corn stalk (CS). As a large agricultural country, China has innumerable crop straw resources, with the highest output for crop straw worldwide; its annual output is about 700 million tons, accounting for 24% of the world's total output, of which CS is approximately 250 million tons, accounting for 41% of the total output of crop straw (Privas and Navard 2013; Li *et al.* 2019). CS is used as a fuel and feed, as well as for panels, *etc.* (Widyorini *et al.* 2005a; Mancera *et al.* 2012; Nagarajan *et al.* 2013; Yuan *et al.* 2019). However, straw is currently found widely in several industrial outlets due to the decline in its demand and prices over the past 15 years. Developed countries as well as countries with high demand for agricultural modernization are increasing their attention to the recycling and full use of crop straw to promote agricultural resource utilization and environmental protection (Mancera *et al.* 2012; More 2021).

Along with China's economic development and accelerating pace of agricultural modernization, steady development of the rural economy and society, a considerable change in the farmers' way of life, and a fundamental change in agricultural production,

crop straw is rarely used in wet compost and cooking, which is used less than 5%. The problem of straw overstocking in rural areas is difficult to handle. Incineration of straw *in situ* causes serious air pollution and other environmental problems, as well as wastage of these resources (Ravindra *et al.* 2019). To solve the above problems and enhance the added value of straw-derived products, straw treatment technology is being developed. Crops comprise a high amount of a wax layer and ash on their surface due to growth characteristics, making their utilization difficult (Li *et al.* 2010). The surface treatment of straw raw materials reduces the effects of different components such as silicon and other mineral content on the bonding phase and substrate, and the interface compatibility between straw and the bonding phase can be improved (Zhang *et al.* 2003).

Pretreatment technologies include mechanical treatment (Yousefi 2009), humid heat and steam treatment (Widyorini *et al.* 2005b; Kaushik *et al.* 2010), biological treatment (Zeng *et al.* 2011; Ko *et al.* 2019), chemical treatment (Martelli-Tosi *et al.* 2017; Lazorenko *et al.* 2020), and physical treatment (Li *et al.* 2012). There are two problems with traditional pretreatment methods: (1) physical methods such as heat treatment and steam blasting not only destroy the surface structure of straw but also reduce the strength of straw to a certain extent; (2) biological methods have a long cycle and high costs. Related research has focused on kenaf, soybean, and wheat straw materials (Zhang *et al.* 2003; Kalaycioglu and Nemli 2006; Ye *et al.* 2007; Nyambo *et al.* 2010; Tabarsa *et al.* 2011), while CS has been investigated to a relatively low extent (Wang and Sun 2002; Zhou *et al.* 2010; Wu *et al.* 2011). Hence, it is crucial to seek efficient green pretreatment methods for CS.

In this study, CS was selected as the raw material, and oxalic acid, oxalic acid + ultrasound, NaOH, and NaOH + ultrasound were selected as pretreatments. The changes in the chemical composition, surface elements, aggregation structure, and microstructure of CS were investigated to select suitable pretreatment methods, which might serve as a theoretical guide for further research and practice.

EXPERIMENTAL

Materials

Corn stalks obtained from Anda (Heilongjiang Province, China) were reduced into smaller particles using a flaker (FW-100 high-speed shredder, Changzhou, China). The obtained particles were dried to a moisture content of 5% and passed through a 40- to 60-mesh sieve for separation. Pure analytical-grade oxalic acid and NaOH were purchased from Tianjin Guangfu Chemical Reagent Co., Ltd. (Tianjin, China).

Table 1. Experimental Design of Corn Stalk Pretreatment

No.	Sample	Method	Condition
1	Control	-	-
2	CS _E	5% Oxalic Acid	50 °C for 1 h
3	CS _{EUS}	5% Oxalic Acid	Ultrasonication at 50 °C for 1 h
4	CS _N	5% NaOH	50 °C for 1 h
5	CS _{NUS}	5% NaOH	Ultrasonication at 50 °C for 1 h

Methods

Pretreatment of corn stalks

The effects of oxalic acid, oxalic acid + ultrasound, NaOH, and NaOH + ultrasound pretreatment on the waxy layer and SiO₂ on the CS surface were investigated. Table 1 shows the specific experimental design. First, 3 g of CS was dispersed into a 5% oxalic acid or a NaOH solution to form a slurry with a 3% mass concentration. Pretreated CS was dried at 60 °C for 24 h after mechanical stirring at 50 °C or ultrasonication for 1 h. The ultrasonic treatment was carried out by an ultrasonic cleaning (KQ-300DE ultrasonic cleaning machine, Kunshan, China). The CS was treated with ultrasonic wave of 300 W at 50 °C for 1 h in the ultrasonic volume of 10 L. The control group represented CS without pretreatment. Oxalic acid pretreatment, oxalic acid + ultrasound pretreatment, NaOH pretreatment, and NaOH + ultrasound pretreatment were referred to as CS_E, CS_{EUS}, CS_N, and CS_{NUS}, respectively.

GC-MS analysis

Organic components of CS under different pretreatment conditions were investigated by gas chromatography-mass spectrometry (GC-MS). Chloroform was used for extraction. One microliter of the sample was automatically injected with a split ratio of 2:1 and a split flow rate of 1 mL/min. The inlet temperature was set to 280 °C. The oven was programmed for ramp from 130 to 320 °C at a ramp rate of 10 °C/min and maintained constant at 320 °C for 18 min. The resulting mass spectrum was analyzed using the NIST 20 Library.

Surface characterization of CS

X-ray photoelectron spectroscopy (XPS) was employed to scan the surface chemistry of CS before and after pretreatment, and changes in the C, N, O, and Si content on the sample surface were measured. Table 2 summarizes the chemical shifts and existing valence states of relevant elements. XPS analysis was conducted using MgK (1253.6 eV) as the X-ray source at a pass energy of 20 eV and a vacuum degree for the analysis room of 3.2×10^7 Pa.

Table 2. Chemical Shifts and Structures of Surface Elements of Samples

Element	Electronic Orbit	Element State	Binding Energy (eV)	Chemical Shift
C	1s	C1: C–C, C–H	285.0	0
		C2: C–O	286.5	1.5
		C3: C=O, O–C–O	288.0–288.5	3.0–3.5
O	1s	O–H–O	534.3	2.4
		O–C=O	533.41	1.414
		C=O	533.15	1.15
		O–C	532.64	0.64
Si	2p	Si	99.1	0
		SiO ₂	103.2	4.2
		Si–C	99.7	0.6
		Si ₃ N ₄	96.5	0.4

FTIR and XRD analyses

Fourier transform infrared (FTIR; Thermo Fisher Scientific, Waltham, MA, USA) spectroscopy was employed to analyze changes in functional groups of the samples. The KBr tablet method was employed, and powder samples were used. FTIR spectra were

recorded from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} , with a scanning time of 40. X-ray diffraction (XRD) was employed to analyze the crystal structure and relative crystallinity of the samples. The scanning range was 5° to 50° at a scanning speed of 5°/min, and the step distance was 0.02°. The crystallinity index of the sample was calculated in accordance to a previous study (Segal *et al.* 1959).

Surface morphological analysis

Scanning electron microscopy (SEM) images were recorded to evaluate morphology changes of the CS surface under different pretreatments on a Sirion 200 instrument (FEI, Hillsboro, Oregon, USA). The samples were sprayed with gold to increase the conductivity of the samples. The high-vacuum mode was adopted for tests, and SEM images were recorded at a beam voltage of 12.5 kV.

RESULTS AND DISCUSSION

Analysis of Wax Compounds of the CS Surface after Pretreatment

As key components of the water barrier, epidermal waxy CS was attached to the outermost layers of the plant hydrophobic material (Bourgault *et al.* 2019). According to GC-MS analysis, the wax compounds of CS under different pretreatment conditions were well isolated. From the mass spectrometry database, a total of 16 epidermal wax compounds were identified, including alkanes, primary alcohols, aliphatic aldehydes, fatty acids, and diketones (Liao *et al.* 2021). Among these compounds, four alkanes were present, mainly with an odd number of carbon atoms with a carbon chain length of C₂₅–C₃₁ alkanes. Four primary alcohols were present, mainly with even carbon atoms and carbon chain lengths ranging from C₂₂ to C₃₀. Six fatty acids, mainly with an even number of carbon atoms and carbon chain lengths ranging from C₂₂ to C₃₂, were present. Two diketones, *viz.* β -diketones with a carbon chain length of C₃₁ and their derivatives. Figure 1 shows the quantitative analysis of the total wax layer and contents of each component in the control, C_{SE}, C_{SEUS}, C_{SN}, and C_{SNUS}. Compared to the control (11.26 $\mu\text{g}/\text{cm}^2$), the total wax content decreased in the order of C_{SNUS} > C_{SEUS} > C_{SN} > C_{SE}. Fatty acids were the main wax components of the outer surface of CS, and the fatty acids of the control, C_{SNUS}, C_{SEUS}, C_{SN}, and C_{SE} reached 9.86, 3.66, 3.89, 4.16, and 5.37 $\mu\text{g}/\text{cm}^2$, respectively.

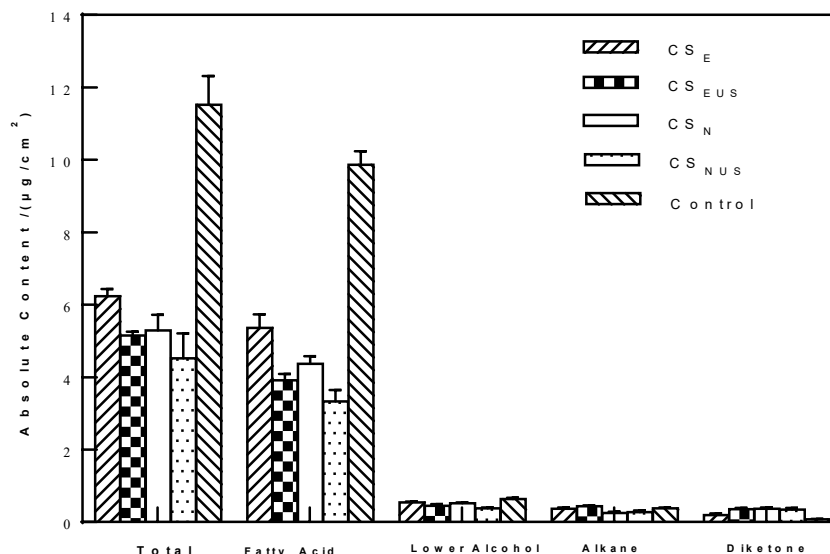


Fig. 1. Absolute content of the total wax and components of corn stalk after various pretreatments

Table 3. Relative Contents of Wax Components of Corn Stalk

Wax Components	Pretreatment Condition (%)				
	Control	CS _E	CS _{EUS}	CS _N	CS _{NUS}
Fatty acid	87.56±2.19	83.22±1.03	77.9±3.40	79.45±2.11	78.24±2.26
Lower alcohol	7.39±1.76	7.97±0.48	6.98±1.17	9.24±0.72	8.36±0.80
Alkane	4.13±0.67	5.89±0.88	8.89±0.21	4.76±1.02	5.94±1.71
Diketone	0.92±0.24	2.92±0.63	6.23±2.02	6.55±1.81	7.46±0.25
Total	100	100	100	100	100

The relative content of epidermal wax components of CS raw materials revealed 87.6% of fatty acids, followed by 7.4% of primary alcohols, 4.1% of alkanes, and 0.92% of diketones. The wax components of CS epidermis were different under different pretreatment conditions. The fatty-acid content of wax exhibited a decreasing trend, and the relative contents of fatty acids reached the minimum after the oxalic acid + ultrasound treatment. The primary alcohol and alkane content increased marginally and reached the maximum after NaOH and oxalic acid + ultrasound treatments. The relative content of dione increased, while the dione content reached the maximum after the NaOH + ultrasound treatment. The results revealed that the effect of the pretreatment of the wax layer of the CS surface is particularly important to improve wettability on the straw surface.

Effect of Pretreatment on Chemical Elements and Lignin Content of CS

X-ray photoelectron spectroscopy is an efficient modern analytical method to characterize the chemical composition of material surfaces (Popescu *et al.* 2009). Unlike wood, CS contains a certain amount of a wax layer and Si on its surface, in addition to the three main components (*i.e.*, cellulose, hemicellulose, and lignin). The distribution and valence states of C, O, Si, and N in CS were determined. The O/C ratio on the CS surface was calculated by XPS spectroscopy at a low resolution, and the relative content of C1s in different oxidation states was calculated by XPS at a high resolution to further determine changes in the lignin content on the CS surface. Figure 2 shows low-resolution spectra of the control, CS_E, CS_{EUS}, CS_N, and CS_{NUS}.

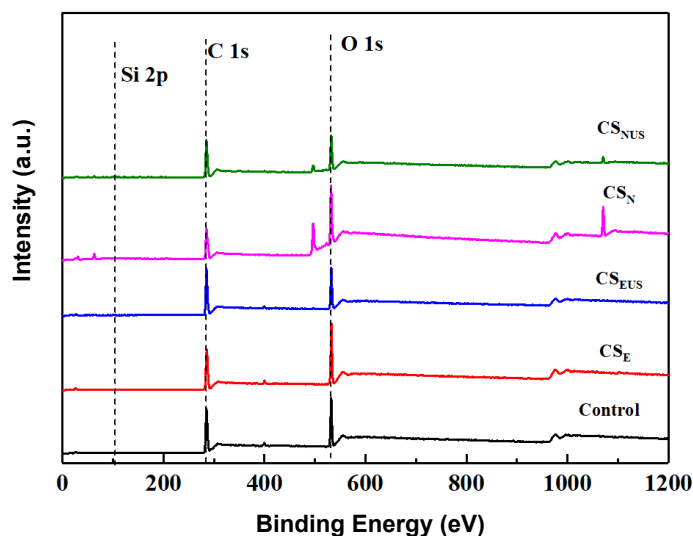


Fig. 2. Low-resolution spectra of C1s, O1s, and Si 2p of corn stalk after various pretreatments

Table 4. Surface Element Content and O/C Ratio of Corn Stalk after Various Pretreatments

Samples	Oxygen Total (%)	Carbon Total (%)	Atomic Ratio (O/C)	Si Total (%)	N Total (%)
Control	26.34	69.94	0.37	1.23	3.23
CS _E	31.07	65.41	0.48	0.66	2.86
CS _{EUS}	23.67	72.53	0.33	0.60	2.67
CS _N	38.61	59.58	0.65	0.84	0.97
CS _{NUS}	26.19	71.70	0.37	0.73	1.38

Table 4 shows the surface elemental contents of each sample. Compared with the O/C ratio of the control, the O/C ratios of oxalic acid and NaOH pretreatment were higher, indicative of a low lignin content of CS_E and CS_N. The higher O/C ratio on the CS surface may be related to the dominant effect of the depolymerization of lignin on the CS surface (Ström and Carlsson 1992). However, the O/C ratio did not change significantly in synergistic ultrasound treatment, indicating that ultrasound treatment does not affect the lignin content on the CS surface. For Si, the chemical environment of Si in the sample was mainly in the form of SiO₂ (binding energy of 103.2 eV). Pretreatment could effectively reduce the content of SiO₂ in the straw, and the reduction degree followed the order of CS_{EUS} > CS_E > CS_{NUS} > CS_N. Compared with that in the control, the N content of all pretreated samples reduced, and that of CS_N was the least, possibly because NaOH could remove protein compounds in CS, leading to the reduction of N.

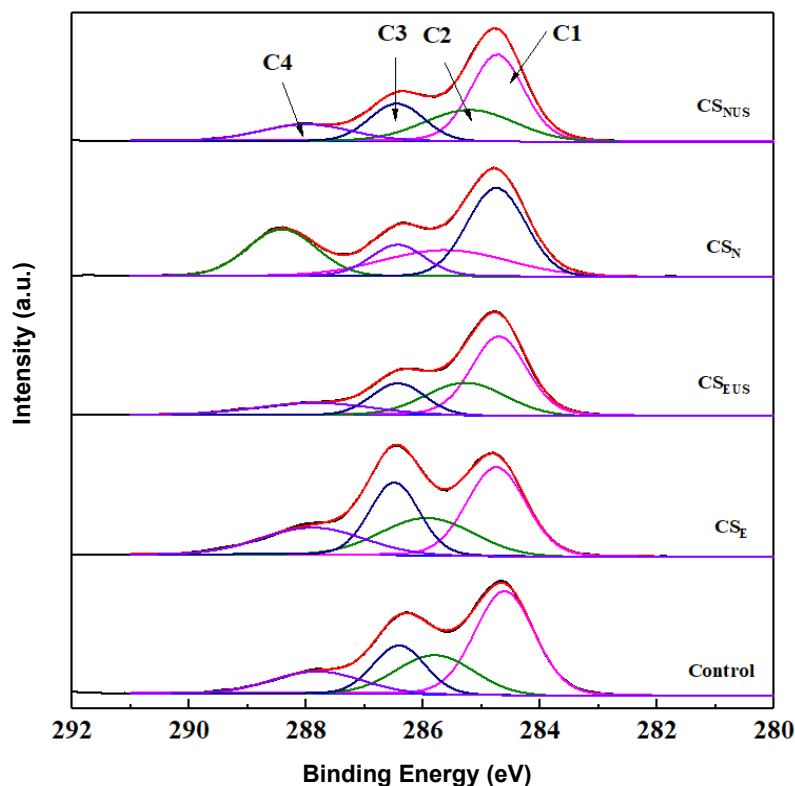


Fig. 3. High-resolution spectra of C1s of corn stalk after various pretreatments

Table 5. Binding Energies and Peak Area of Samples

Samples	Binding Energy (eV)				Peak Area (%)			
	C1	C2	C3	C4	C1	C2	C3	C4
Control	284.6	285.7	286.4	287.8	46.62	21.49	18.15	13.75
CS _E	284.7	285.9	286.5	287.8	35.70	22.26	24.49	17.56
CS _{EUS}	284.6	285.3	286.4	287.8	45.97	25.18	16.11	12.74
CS _N	284.7	285.6	286.4	288.4	38.86	24.25	13.38	23.50
CS _{NUS}	284.7	285.2	286.4	288.0	44.15	25.15	17.85	12.84

The high-resolution C1s spectra of corn straw under different pretreatment conditions were fitted (Fig. 3). Table 5 summarizes the C1–C4 chemical binding energies and relative absorption peak area of C1s with different oxidation states. The relative absorption peak area of C1 (C–C and C–H only exist in lignin or in the extract of CS but not in cellulose and hemicellulose) in the control was 46.6%. The peak area of CS_E, CS_{EUS}, CS_N, and CS_{NUS} decreased to 35.7%, 46.0%, 38.9%, and 44.2%, respectively. Compared to CS_E and CS_N, CS_{EUS} and CS_{NUS} exhibited lower C1 peak areas, indicating that oxalic acid + ultrasound and NaOH + ultrasound treatments can remove a small amount of lignin from the CS surface; this result is consistent with that of the reduction of lignin content in the low-resolution spectrogram. The peak area of C2 (C–O, which exists in carbohydrate components of CS), increased after different pretreatments compared to the control, indicating that carbohydrate on the CS surface increase after pretreatment and that the increasing increase degree in the order of CS_{EUS} > CS_{NUS} > CS_N > CS_E. The peak area of C3 (C=O or O–C–O) increased only in CS_E after different pretreatments compared to the control, which may be related to the oxalic-acid degradation of cellulose/hemicellulose in

CS. The peak area of C4 (O-C=O, mainly in carboxylic acid) decreased compared to the control, CS_{EUS}, and CS_{NUS}, and it increased in CS_E and CS_N. These results are thought to be related to the increase in the carboxylic-acid components in the sample during pretreatment and the fact that ultrasound treatment potentially remove a part of the carboxylic-acid components, leading to two changes in the carboxylic acid components (Popescu *et al.* 2009).

Analysis of Chemical Components of CS after Pretreatment

The chemical compositions of samples were determined according to GB/T 2677. Compared with that of wood, the main chemical composition of CS was similar to that of poplar and broadleaf forest (Yuan and Guo 2017), but its ash content and extract content were greater than that of wood (Rodríguez *et al.* 2010). Compared with other crop straws, corn straws exhibited a higher lignin content (Reddy and Yang 2005). Changes in the main chemical components on the CS surface before and after pretreatment were observed (Table 6).

Table 6. Main Chemical Components of Samples

Samples	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Extract Solution (%)				Ash Content (%)
				Cold Water	Hot Water	Benzyl Alcohol	1% NaOH	
Control	25.32	46.23	26.76	6.23	12.78	3.72	35.65	1.44
CS _E	24.69	54.23	20.76	6.09	10.24	2.76	37.52	1.04
CS _{EUS}	20.76	55.72	20.13	4.47	8.65	1.62	33.67	0.52
CS _N	16.13	59.78	22.41	6.14	11.62	2.46	35.24	1.05
CS _{NUS}	10.26	62.79	23.64	5.05	9.72	1.24	32.91	0.74

The contents of ash and solution extract considerably affected the production of non-wood-based panels. Ash is an inorganic residue of straw after high-temperature combustion, and SiO₂ is its main component. A high ash content not only causes dust pollution but also increases the cost of adhesive raw materials. The cold-water extract mainly contains tannins, pigments, alkaloids, soluble mineral components, and some sugars, while the benzene-alcohol extract mainly contains oils, waxes, and fats, as well as a small number of soluble tannins and pigments. The 1% NaOH extract contains protein, amino acid, and a small amount of oil, wax, and essential oil, in addition to the components of the hot-water extract. The higher the solution extract content, the more difficult the bonding with the adhesive, and the size deviation of the panel can easily occur. Moreover, with long-term storage, rotting can easily occur, and mildew and moisture again affect the composite panel, which in turn affects its performance. Compared to the control, the benzene-alcohol extract and ash content decreased after pretreatment, which was consistent with the results obtained from GC-MS and XPS; this result indicated that pretreatment can be an effective to treat the wax layer and ash content of CS.

The main characteristic peaks observed in the IR spectrum of the CS surface were as follows (Fig. 4): 3317 to 3331 cm⁻¹ corresponding to OH stretching, which is generally thought to represent cellulose, hemicellulose, and polysaccharide monosaccharide; 2888 to 2904 cm⁻¹ corresponds to the anti-symmetric peak of -CH stretching vibration in cellulose; 1640 to 1730 cm⁻¹ corresponds to the C=O stretching vibration peak of lignin or

hemicellulose-related carboxylic esters and ketones. The C-O-C asymmetric stretching vibration peak of aliphatic compounds was observed at 1159 cm^{-1} , and the Si-O stretching vibration of inorganic materials such as SiO_2 was observed at 1016 cm^{-1} . A significant change in the IR spectra of CS after pretreatment was not observed, indicating that it does not significantly affect the principal components of CS and that it plays a role in surface removal rather than in modification.

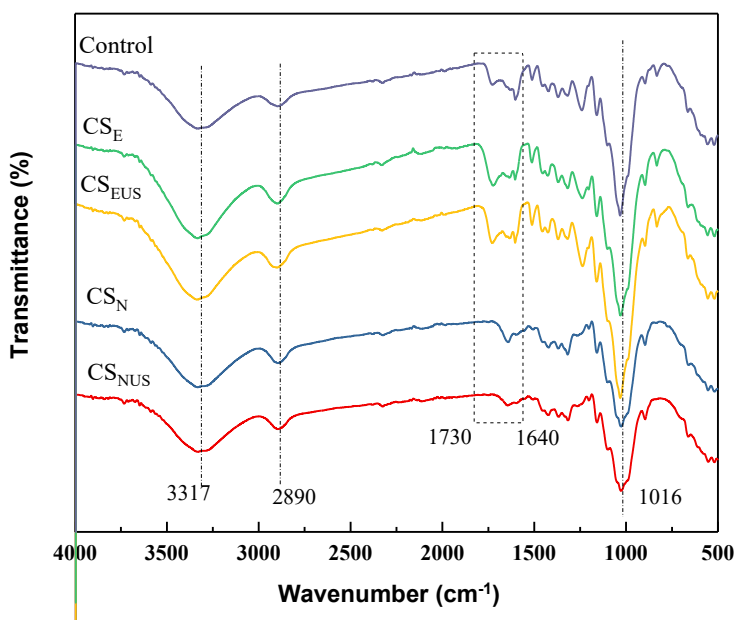


Fig. 4. FTIR spectra of corn stalk surface after pretreatment

Compared with untreated CS, some characteristic absorption peaks on the CS surface without pretreatment were changed. After four types of pretreatment (*viz.* oxalic acid, oxalic acid + ultrasound, NaOH, and NaOH + ultrasound, respectively), the intensity of absorption peaks corresponding to OH stretching and C-H stretching vibrations increased, and the amplitude of enhancement decreased in the order of $\text{CS}_N > \text{CS}_{\text{NUS}} > \text{CS}_E > \text{CS}_{\text{EUS}}$, which may be oxalic acid + ultrasound caused to the cellulose structure least damage. After NaOH treatment, the number of bands decreased most clearly at 1640 to 1730 cm^{-1} , which basically disappeared at 1728 cm^{-1} , indicating that NaOH treatment destroys C-O and dissolves lignin and hemicellulose; hence, cellulose content increases (Pang *et al.* 2012). The absorption vibration peak of CS treated with oxalic acid, oxalic acid and ultrasound increased slightly at 1640 to 1730 cm^{-1} , indicating that oxalic-acid treatment could increase the relative contents of hemicellulose and lignin. After pretreatment, compared to the untreated CS surface, the intensity of the peaks was weakened, *i.e.*, bands were observed at 1159 cm^{-1} and 1064 cm^{-1} , and the order was as follows: $\text{CS}_N > \text{CS}_{\text{NUS}} > \text{CS}_E > \text{CS}_{\text{EUS}}$. The results revealed that the oxalic acid + ultrasound pretreatment could effectively reduce the lipid and SiO_2 on the CS surface, thus reducing the waxy layer and ash content on the CS surface and improving its wettability; this result is consistent with those of GC-MS and XPS.

Changes to Crystallinity and Microstructure of CS after Pretreatment

Figure 5 shows changes in the crystal shape and crystallinity of CS before and after pretreatment. Diffraction peaks were observed at 2θ equal to 18.8° and 22.1° , corresponding to typical cellulose I. Therefore, in pretreatment, irrespective of the addition of oxalic acid or NaOH, CS can maintain the integrity of the original crystal, and its diffraction peak is similar to that of natural cellulose (Yao *et al.* 2008). The crystal structure of CS did not change significantly before and after pretreatment. The crystallinity of the CS of control was 55.3%. The crystallinities of CS_E , CS_{EUS} , CS_N , and CS_{NUS} were 62.22%, 64.10%, 60.06%, and 60.83%, respectively. This result indicated that the oxalic acid + ultrasound pretreatment is suitable for the growth of crystallinity; meanwhile, a positive effect on the CS lignin-activated treatment was observed.

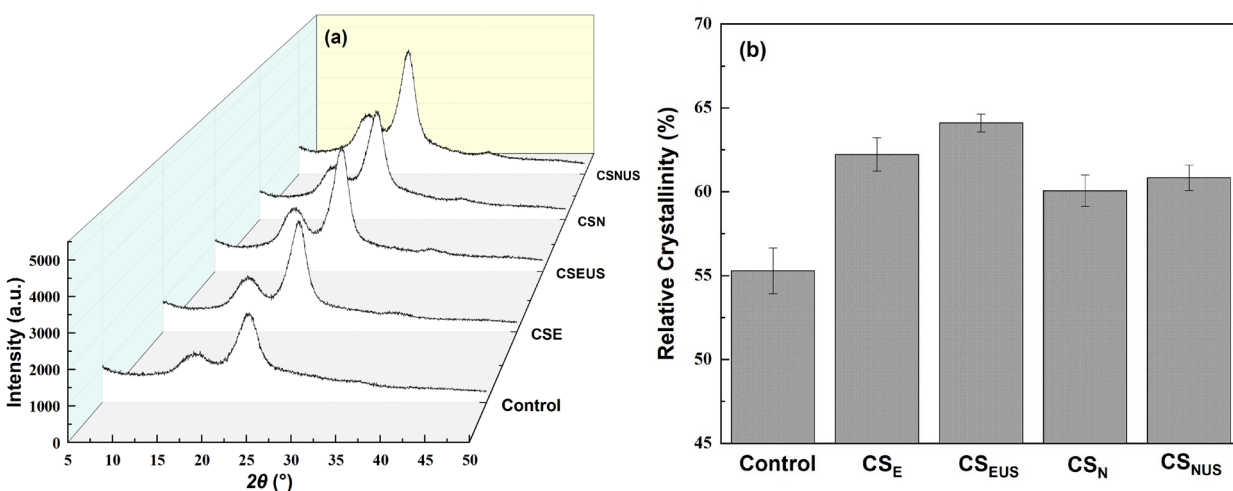


Fig. 5. XRD patterns and relative crystallinity of corn stalks after pretreatment

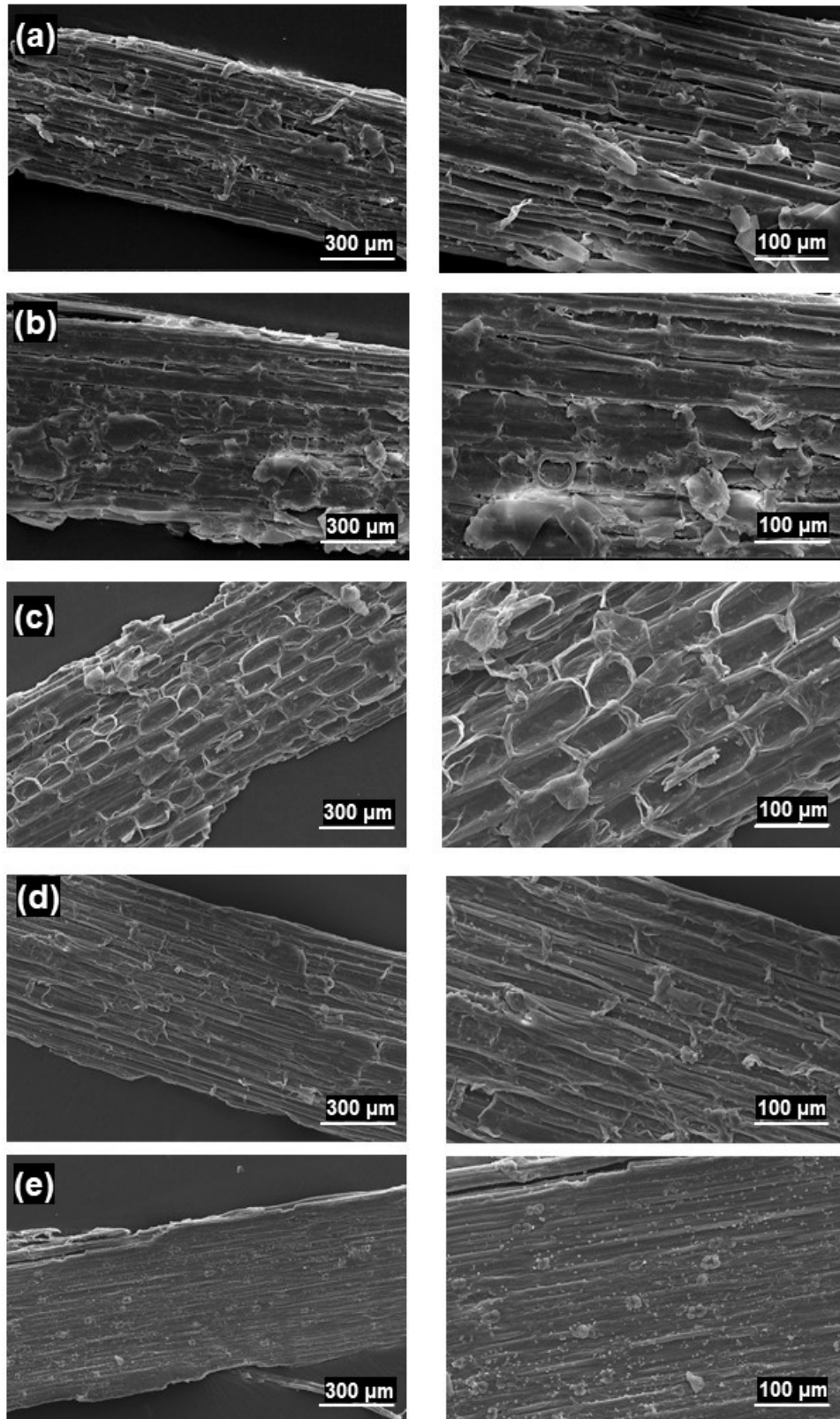


Fig. 6. SEM images of corn stalks before and after pretreatment (a: untreated corn stalks, b: oxalic acid treatment, c: oxalic acid + ultrasonic treatment, d: NaOH treatment, e: NaOH + ultrasonic treatment)

The outer surface of CS without pretreatment was dense and smooth, and the surface wax layer was clearly visible (Fig. 6). After oxalic acid and oxalic acid + ultrasound pretreatments, the surface gloss of CS decreased, indicating that the cuticle and siliceous layers are partially removed, albeit the overall surface is relatively smooth. After oxalic acid + ultrasound pretreatment, the approximately rectangular thin-walled cells on the inner surface of CS were exposed clearly, similar to enzymatic treatment (Ko *et al.* 2019). After NaOH and NaOH + ultrasound treatment, the silky layer on the CS surface was almost dissolved, and the fibers were exposed. Notably, after NaOH + ultrasonic treatment, a part of flower-like SiO₂ was broken and dispersed on the CS surface, further confirming that pretreatment can remove lipid substances on the CS surface, which is consistent with the results obtained from GC-MS, XPS, and FTIR.

CONCLUSIONS

1. Compared with the control, the benzene-alcohol extract and ash content decreased after pretreatment. Si in the samples was mainly present as SiO₂. Pretreatment effectively reduced the SiO₂ content of corn stalk (CS), and the reduction followed the order of CS_{EUS} > CS_E > CS_{NUS} > CS_N, where the subscripts have the following meanings: E = oxalic acid extraction; US = ultrasonic treatment; N = NaOH extraction
2. Four pretreatments effectively reduced the waxy layer and ash content on the corn straw surface and improved its wettability. The total amount of wax decreased in the order of CS_{NUS} > CS_{EUS} > CS_N > CS_E. Fatty acids were the main wax components of the outer surface of corn stalk. The crystallinity of CS was clearly improved after pretreatment in the following order: CS_{EUS} > CS_E > CS_{NUS} > CS_N.
3. The optimal pretreatment conditions of CS were oxalic acid + ultrasound treatment, *i.e.*, 5% oxalic acid and ultrasound treatment at 50 °C for 1 h.

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