Ionic liquid depolymerize the lignocellulose for the enzymatic extraction of feruloylated oligosaccharide from corn bran

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ABSTRACT

In this study, a new method was developed for feruloylated oligosaccharides (FOs) enzymatic hydrolysis extraction from corn bran, using ionic liquids (ILs) as the solvent for the depolymerization of dietary fiber. The 1-allyl-3-methylimidazolium acetate [Amim]Ac was the most effective IL among the eight evaluated ILs, which leads to a 1.5 times-higher total FOs content as compared with conventional non-pretreatment extraction. The optimum condition acquired by response surface methodology was 194.31 min, 143.08 °C, solid–liquid ratio of 1:20, and the concentration of 18.65%. The depolymerized biomass was characterized using SEM, FTIR and CLSM. The results confirmed that [Amim]Ac mainly enters the cavity among the lignocellulose and breaks linkages to release FOs by exposure binding sites of hemicellulose to hydrolysis enzymes. In particular, the linkages between ferulic acid and hemicellulose were not affected by ILs pretreatment. This study provides an efficient method for the preparation of conjugated phenols from lignocellulose.

Introduction

Feruloylated oligosaccharide (FOs), as a representative functional ingredients obtained from cereal bran such as wheat bran, rice bran, and corn bran, is formed by the ester bond between the carboxyl group of ferulic acid (FA) and the O-5 position of the hydroxyl end of the arabinoxylan (AX) side chain and the ether bond is cross-linked with lignin (Wang, Baoguo, Yanping, & Yuan, 2009). FA bridges cross-linking between hemicellulose molecular chains and between two polymer molecules, namely, hemicellulose and lignin. Due to the combined actions of oligosaccharides and FA moieties, FOs exhibit higher health-promoting effects than FA (Masuda et al., 2000), such as the antioxidant activity, anti-glycosylation (Wang et al., 2009), alleviate diabetic syndrome (Song et al., 2020), probiotic effect (Gudipati, Schwarz, Dobleit, Fuhrmann, & Krueger, 2011), inhibition of nonenzymatic glycosylation (Silvan, Assar, Srey, Dolores del Castillo, & Ames, 2011), immune regulation, antitumor function and prebiotic effects (Gong et al., 2019). In 2010, FOs has been approved by the FDA as a food additive (GRAS NOTICE 000343). However, the application of FOs in food industry is limited due to its low extracting yields from the natural fiber materials. Corn is one of the three major food crops in the world. Based on corn production data in China, the annual output of corn bran is 30 million tons. Upgrading corn barn could create additional value and help develop functional dietary ingredients. The progresses of extracting technology that can selectively degrade substituted arabinoxylans have provided a favorable basis for producing FOs from corn brans. These technologies include acid hydrolysis, enzymatic hydrolysis, high-pressure cooking and biological fermentation that result in the hydrolysis of the glycosidic bonds of the xylan chain and severing of the high branches and bridges of cellulose or lignin (Bai, Sun, Wang, & Wang, 2017). However, the complex crosslinking between cell wall polysaccharide and ferulates result in low extraction yields of FOs. Many pretreatment methods have been developed to meet this objective, Compared with the untreated group, The extraction yield of FOs was increased by sonication (Katapodis & Christakopoulos, 2008), high-pressure cooking (Xie et al., 2016), mechanical ball milling treatment (Zhang, You, Cai, & Cao, 2015) up to 50%, 42%, 36.14% respectively. In addition, the FOs extraction rate can reach about 60% by microwave assisted processing (Rose & Inglett, 2010) and pressurized hot water (Pazo-Cepeda, Aspromonte, & Alonso, 2021). Therefore, the addition of a one-step pretreatment before the basic extraction process of FOs can improve the accessibility of the raw material cell wall and play an important role in the improvement of subsequent studies (Niemi et al., 2012).

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Ionic liquid (IL) is a liquid organic salt that consists of an organic cation paired with an organic or inorganic anion. It is an environmentally friendly 'green' solvent due to its advantages of negligible vapor pressure, non-flammability, high thermal stability and low toxicity (Huddleston et al., 2001). ILs have high polarity, making them have potential to depolymerize and dissolve lignocellulosic biomass (Hu et al., 2020; Silva, 2021). Notably, ILs consisting of an imidazole cation proved to be an effective pretreatment solution for lignocellulose (Roy & Chundawat, 2022; Xia et al., 2020), and could form new chemical bonds with hemicellulose and effectively destroy the three-dimensional network structure, weaken intermolecular and intramolecular hydrogen bonds, loosen the structure, and reduce the degree of polymerization and crystallinity (Elgharbawy, Alam, Moniruzzaman, & Goto, 2016; Yoo, Pu, & Ragauskas, 2017). The commonly used anions are mainly conjugates of strong acids, such as Cl⁻, Br⁻, and CH_3COO^- (Zhang, Xu, & Yin, 2019).It is reported that pretreated bagasse with 1-ethyl-3-methylimidazolium acetate lead to reducing the size of the bagasse and increasing its surface area by 100 times (Lee, Doherty, Linhardt, & Dordick, 2009). The yield of reducing sugars reached more than 90% after enzymatic hydrolysis for 24 h. [Emim]Ac effectively pretreated wood flour at 80 °C for 1 h, making its structure more porous and greatly improving the enzyme degradation efficiency without damaging the biomass macromolecular components (Moniruzzaman & Ono, 2013). This conclusion was also found by Monica, who found that no true separation of cellulose, hemicellulose and lignin occurred after pretreatment of wheat bran with [Emim]Ac (Araya-Farias et al., 2019). Therefore, the aim of this study was to explore the collapse effects of ILs on corn bran lignocellulose which may improve the enzymatic hydrolysis to release FOs. Briefly, eight ILs were used for pretreatment depolymerization of lignocellulose. The chemical properties of lignocellulose were characterized by infrared spectroscopy, scanning electron microscopy and confocal laser microscopy. The FOs extracted from ligoncellulose was carried out with and without pretreatment of ILs, and meanwhile compared the results with conventional enzymatic hydrolysis. To our knowledge, no antecedent work has been reported on the use of ILs to facilitate the release of FOs. Hence, proving the ILs pretreatment effectiveness would offer an entire new solution for industrial production of FOs.

Materials and methods

Materials

Corn bran was obtained from Tianjin Tianhua Chemical Industry Group Co., Ltd. (Tianjin Province, China). 1-Ethyl-3-methylimidazole acetate ([Emim]Ac),1-Ethyl-3-MethylImidazolium Chloride ([Emim] Cl),1-Ethyl-3-MethylImidazolium formate ([Emim]HCOO),1-Butyl-3-methylimidazolium chloride ([Bmim]Cl),1-Allyl-3-methylimidazolium chloride ([Amim]Cl),1-Allyl-3-methylimidazolium formate ([Amim] HCOO),1-Allyl-3-methylimidazolium acetate ([Amim]Ac),and 1-Propyl-3-methylimidazolium chloride ([Pmim]HCOO)were obtained from Shanghai Chengjie Co., Ltd (Shanghai Province, China). Xylanase was purchased from Wuhan Xinhua Yang Biological Co., Ltd (Wuhan Province, China). Neutral protease was purchased from Beijing Aoboxing Biotechnology Co., Ltd. Amylase- and high-temperature-resistant α-amylase were purchased from Beijing Solaibao Co., Ltd. (Beijing Province, China).

Preparation of maize bran insoluble dietary fiber

The corn dietary fiber was obtained according to the method of Rose et al. with some modifications (Rose & Inglett, 2010). One hundred grams of corn bran was grinded and passed a 40-mesh sieve. To inactive the endogenous enzymes, the bran was treated at 121 °C for 45 min, then deionized water was added and then stirring at 60 °C for 24 h to fully swell it. Next, 275 mol/L NaOH was added to adjust pH to 7.0 and

high-temperature resistant α-amylase was added (100 °C for 30 min). After cooling, the pH was adjusted to 10.0 and alkaline protease (60 °C for 30 min) was added. Then the pH was adjusted to 4.5 with 325 mol/L HCl, and the saccharifying enzyme was added (60 °C for 30 min). Finally, the reactants were freely precipitated, and the supernatant was discarded to remove impurities such as protein and starch. Hot and cold water were used to clean the precipitate until the supernatant had no obvious turbidity. The supernatant was washed with alcohol and acetone and dried at 45 °C in a vacuum-drying oven to obtain corn insoluble dietary fiber (IDF). At the same time, determination of free, bound and bound ferulic acid in IDF according to the method of Karb et al. with slightly modification (Kalb, Seewald, Hofmann, & Granvogl, 2020).

Ils pretreatment of corn bran IDF

The effects of eight ILs ([Emim]Ac, [Emim]Cl, [Emim]HCOO), [Bmim]Cl, [Amim]Cl, [Amim]HCOO, [Amim]Ac, and [Pmim]HCOO on corn IDF were compared. The most suitable IL solvent was then selected to pretreat corn bran IDF for FOs extraction. The pretreatment of corn bran IDF with selected IL was carried out as follows. An amount of dried IDF was added to ILs for reaction. The supernatant was centrifuged at 10000 rpm at 20 °C for 20 min and washed with ultrapure water 5 times. And the residue was cooled and washed twice with ultrapure water at 20 °C for 30 min to remove the IL before freeze-dried for 24 h to obtain IL-pretreated IDF for enzymatic hydrolysis. The remaining IL-aqueous solution was collected and rotated for recycling. The pretreatment temperature (100, 110, 120, 130, 140, 150 °C), time (40, 80, 120, 160, 200, 240 min), IL concentration (5, 10, 15, 20, 25, 30%), and IDF amount (1.5, 2.0, 2.5, 3.0, 3.5, 5.0 g) were found using single factor experiment.

For enzymatic hydrolysis, a portion of the pretreated-IDF (165 g/L) was dissolved in acetate buffer (50 mol/L, pH 5.0) and mixed with 6 g/L xylanase (4000 U/g), 8 g/L cellulase (4000 U/g). The mixture was incubated on a water bath thermostatic oscillator at 150 rpm and 60 °C for 24 h before filtration. Then, the filtrate was inactivated in a boiling water bath for 10 min and centrifuged at 5000 rpm for 30 min. The filtrate was stored for quantification of FOs after passing through a 0.45 μm microporous ultrafiltration membrane.

Determination of FOs by HPLC

The content of FOs was expressed as mmol ferulic acid per liter solution. The conjugated ferulic acid in FOs was hydrolyzed according to the reported HPLC method (Xie et al., 2010). Briefly, 1 mL of sample solution was added to 1 mL of NaOH (1 mol/L) and hydrolyzed at 100 °C for 90 min. Then, 1 mol/L HCl was added to adjust he pH to 7.0. The molar concentration of FOs was calculated by subtracting the free ferulic acid. A sample of 20 μL was analyzed using an Eclipse Plus C_{18} column (4.6 × 250 mm, 5 μm), at 30 °C with UV detection wavelength was 325 nm. The solvents were 5% trifluoroacetic acid (V/V) (A) and acetonitrile (B), the flow rate was 0.6 mL/min. Gradient elution was performed as follows: 0–15 min, 5–20% solvent B; 15–40 min, 20–40% solvent B; 40–50 min 40–20% solvent B; 50–60 min, 20–5% solvent B; re-equilibrium for 5 min.

Optimization of factor levels by response surface methodology (RSM)

According to the single factor experiment results, the IL concentration, pretreatment time and pretreatment temperature were taken as the test factors. The factors and levels were designed as follows: the pretreatment temperature (120, 140, 160 °C), the pretreatment time (160, 200, 240 min) and the concentration of IL (15, 20, 25%). FOs content was taken as the response value. To avoid systematic errors, the experiments were conducted in a random order.

Observation of the physical and chemical properties of corn bran IDF

IDF was fixed with glutaraldehyde, and the surface of the samples was gold-plated using the sputtering coating method and observed by Scanning electron microscopy (SEM, JSM-7900F, Hitachi of Japan) to establish a clearer relationship between the structural changes caused by pretreatment. The Fourier Transform Infrared spectroscopy (Nicolet IS10, Thermo Fisher Scientific Inc., Madison, USA) spectra of the original and pretreated IDF were analyzed using with KBr pellets within 4000–400 cm^{-1}. The confocal laser scanning microscopy (CLSM, NIKON

Eclipse Ti,Tokyo,Japan) of the original and pretreated IDF were analyzed to visualize the changes of fiber microstructure and the abundance of bound phenolic compounds. The IDFs were dyed with a fluorescent dye solution consisting of 1.0 mg/mL Congo red. IDF structure images were collected at 488 nm excitation, and phenolic compounds showed natural fluorescence at 408 nm excitation (Zhang et al., 2019).
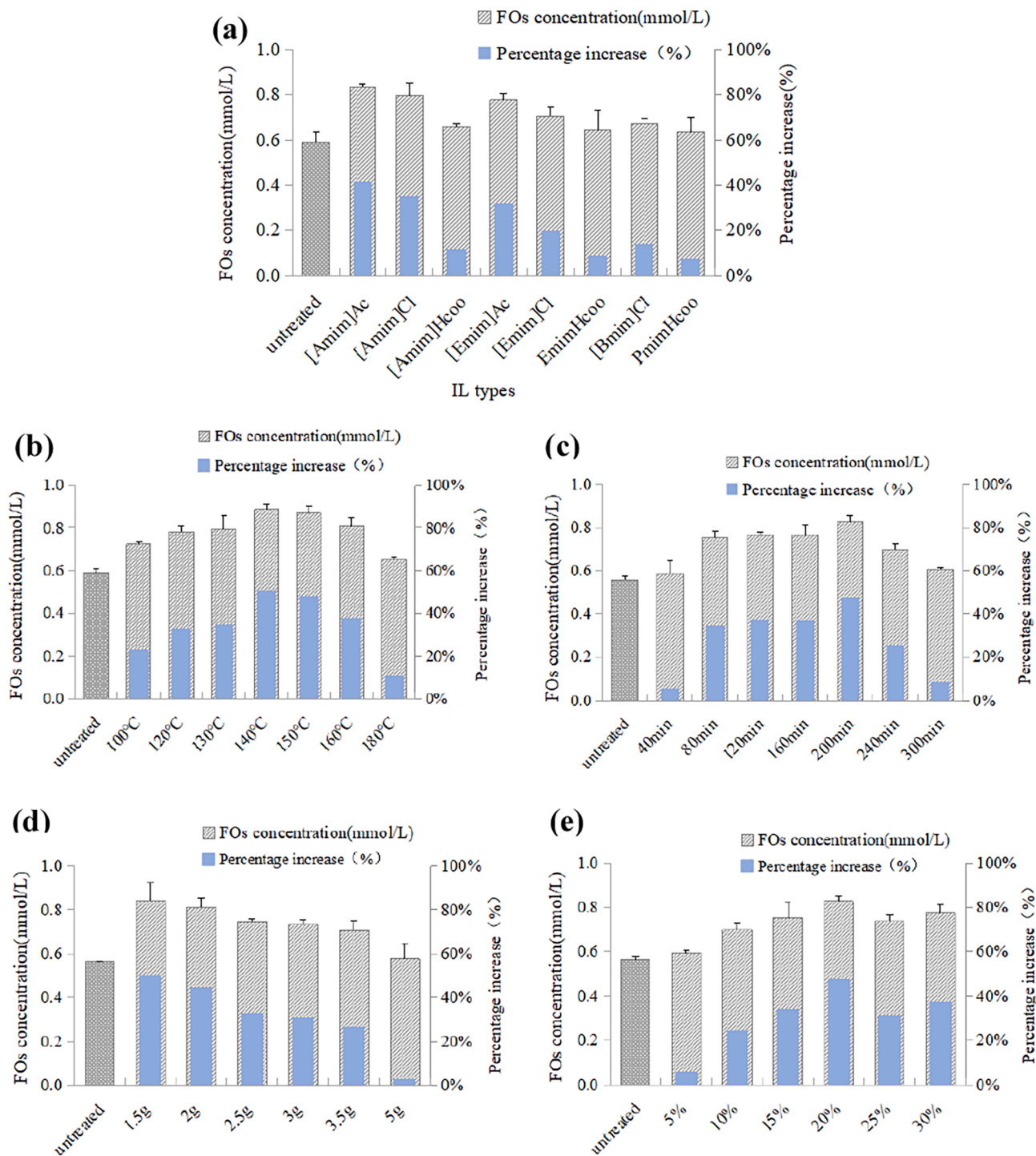

Fig. 1. (a) Effect of IL types on the extraction efficiency of FOs,(b)Effect of pretreatment temperature on FOs concentration,(c) Effect of pretreatment time on FOs concentration,(d) Effect of IDF supplemental amount on FOs concentration,(e) Effect of IL concentration on FOs concentration.

Statistical analysis

Data was presented as mean values with their standard deviation of triplicates. One-way analysis of variance followed by Duncan multiple comparison. was used to analyze the significance of the differences between mean values, with p < 0.05 being defined as statistically significant. Box Benhnken (Version 8.0.6 of Design Expert) was used for the experimental design, statistical analysis and regression model. All statistical analyses were carried out using the STATISTICA program for Windows (Version 7.1, Tibco Software Inc., Palo Alto, CA, USA).

Results and discussion

Selection of the IL for pretreatment of corn bran IDF

In general, the cation and cationic composition of ionic liquid have important effects on its pretreatment performance, which may be influenced by the strength of the bonding with lignocellulose through the intervention of the acid-base of the cation and cationic hydrogen bond (Lethesh, Evjen, Venkatraman, Shah, & Fiksdahl, 2020). In this study, the different cation and cationic effects were selected. As shown in Fig. 1a, the ILs pretreatment of corn bran IDF led to higher FOs yield (increased by 7.47% ~ 40.60%) as compared with un-pretreated IDF. And the extracted yield of FOs from the pretreated IDF was reduced in the order as [Amim]Ac > [Amim]Cl > [Emim]Ac > [Emim]Cl > [Bmim] Cl > [Amim]HCOO > [Emim]HCOO > [Pmim]HCOO. [Amim]Ac was more efficient than [Emim]Ac in the presence of the same anions, which can be due to the conjugate effect of the C=C that makes the group have stronger electron-absorbing ability and stronger hydroxyl binding ability (Wang, Grasvik, Jonsson, & Winestrand, 2017). In addition, under the same cation, the electronegativity of AC⁻ is stronger than that of Cl⁻, in addition to the size effect, which results in different interactions of hydrogen; thus, the screening results are basically consistent with the law. The higher the α (hydrogen bonding acid, cation effect) and β (hydrogen bonding alkaline, anionic effect) values of IL, the stronger the ability to dissolve biomass, which is consistent with the screening results in this study (Sandri, Melo, & Giusti, 2021). [Amim]Ac was selected as the suitable solvent for IDF pretreatment.

Selection of factor levels by response surface methodology (RSM)

Effects of the pretreatment temperature on the extraction of FOs

Fig. 1b indicated that when the pretreatment temperature reaches 140 °C, [Amim]Ac had the best effect on IDF pretreatment, that is, the concentration of FOs is the highest. With increasing pretreatment temperature, the concentration of FOs decreased slightly, which was due to the partial degradation of cellulose hemicellulose, leading to a poor IDF recovery effect. The IDF carbonizes and the ionic liquid decomposed when the temperature is higher than 180 °C, which result in the destruction of the ester bond between lignin and hemicellulose (Zhang, Wei, Yu, & Qiao, 2015).

Effects of the pretreatment time on the extraction of FOs

As seen in Fig. 1c, before the pretreatment time reached 200 min, the concentration of FOs showed an increasing trend, and the percentage increased significantly between 40 min and 80 min. When the pretreatment time was extended to 5 h, the increase in the FOs decreased to 8.43%, which may be due to the degradation of lignin, cellulose and hemicellulose into small molecules with the extension of time, resulting in difficult recovery (Li et al., 2015). Additionally, the prolongation of time may also lead to the cracking reaction of [Amim]⁺.

Effects of the solid–liquid ratio on the extraction of FOs

The influence of the solid–liquid ratio on the FOs concentration is shown in Fig. 1d. As the solid–liquid ratio increases, the concentration of FOs slowly decreases. It is speculated that the increasing initial viscosity

due to pretreatment reduces the mass transfer and diffusion in the system, which hinders the contact between the ionic liquid system and IDF. Especially at a high solid-to-liquid ratio (1:8), a serious rod climbing phenomenon was observed under magnetic stirring, which resulted in the lack of complete immersion of the IDF that was stuck on the bottle wall. Considering the cost-saving for ionic liquid, 1:20 was chosen as the best solid–liquid ratio.

Effects of the ionic liquid concentration the extraction of FOs

As shown in Fig. 1e, ILs pretreatment had little effect when the concentration of ionic liquid was 5%. The FOs concentration increased with the increasing use of [Amim]Ac until the IL concentration reached 20% with the highest FOs. After this, there was an irregular but overall downward trend, which may be due to the effects of the high viscosity of the IL-solvent system that weakening the mass transfer osmotic effect. The results of Kumar et al. also showed that the K-T parameters of the IL, viscosity and surface tension have direct influences on the effect of pretreatment (Raj et al., 2016).

Optimization of factor level by RSM

To further study the interactions between the factors, the 17 experiments shown in Table 1 were carried out randomly and repeated three times. The experimental values of the concentration of FOs were analyzed by multiple regressions to fit the second-order regression equation, and the regression model in terms of coded factors was predicted as follows:

$$Y = +0.83 + 0.018A - 9.25E-3B - 0.026C - 7.5E-4AB + 0.044AC$$
$$+ 0.026BC - 0.028A^2 - 0.058B^2 - 0.047C^2$$

Table 2 shows that the regression model is significant (P < 0.01), and P = 0.0853 (P > 0.05) is not significant, indicating that the model selection is reliable. According to the significance and F value, the order of the influencing factors of IDF pretreatment with IL on the FOs concentration was as follows: ionic liquid concentration > pretreatment temperature > pretreatment time. Considering the interaction between the three factors, the different extraction parameters of multiple nonlinear regression models are shown in Fig. 2(a-c), which depicts the influence of the pairwise interaction of the three factors. After observing the steepness of the response surface, it can be concluded that the interaction between ionic liquid concentration and temperature is strong, while the interaction between ionic liquid concentration and time is slightly weaker, and the interaction between the pretreatment temperature and time is the least strong.

Based on the quadratic model, the optimal combination conditions of

Table 1

Response surface experimental analysis results.

Run	A temperature (°C)	B Time (min)	C IL concentration (%)	FOs concentration (mol/L)
1	−1	0	−1	0.728
2	1	1	0	0.773
3	0	1	1	0.722
4	0	0	0	0.764
5	0	0	0	0.830
6	0	1	−1	0.769
7	−1	−1	0	0.658
8	0	0	0	0.774
9	1	−1	0	0.780
10	−1	0	1	0.698
11	1	0	1	0.706
12	0	0	0	0.729
13	−1	1	0	0.816
14	0	−1	−1	0.836
15	0	−1	1	0.839
16	0	0	0	0.849
17	1	0	−1	0.825

Table 2
The results of variance analysis.

Source	Sum of squares	Degrees of freedom	Mean square	F-value	Prob > F	significance
Model	0.049	9	5.432E-3	12.91	0.0014	**
A	2.521E-3	1	2.521E-3	5.99	0.0443	*
B	6.845E-4	1	6.845E-4	1.63	0.2429	
C	5.513E-3	1	5.513E-3	13.10	0.0085	**
AB	2.250E-6	1	2.250E-6	5.346E-3	0.9438	
AC	7.832E-3	1	7.832E-3	18.61	0.0035	**
BC	2.756E-3	1	2.756E-3	6.55	0.0376	*
A^2	3.39E-3	1	3.390E-3	8.06	0.0251	*
B^2	0.014	1	0.014	33.51	0.0007	***
C^2	9.252E-3	1	9.252E-3	21.98	0.0022	**
Residual	2.946E-3	7	4.209E-4			
Lack of fit	2.292E-3	3	7.640E-4	4.67	0.0853	
Pure error	6.540E-4	4	1.635E-4			
Cor total	0.052	16				

* Significant difference $P < 0.05$; **means The difference is quite significant $P < 0.01$; ***means the difference is extremely significant $P < 0.001$; $R^2 = 0.9432$, $R^2_{adj} = 0.8701$.
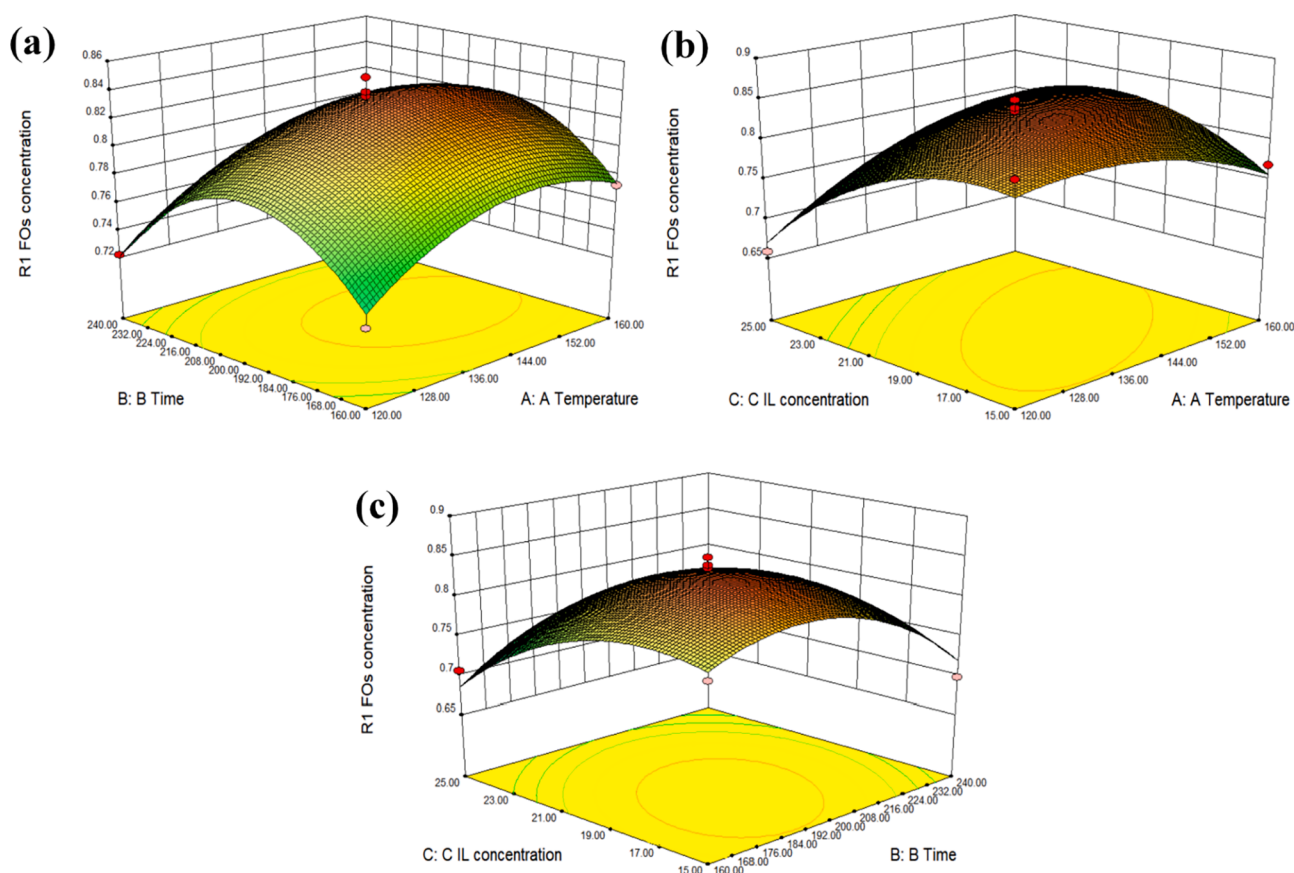

Fig. 2. (a) Response surface diagram of the effect of temperature and time on FOs concentration. (b) Response surface diagram of the effect of temperature and IL concentration on FOs concentration. (c) Response surface diagram of the effect of time and IL concentration on FOs concentration.

IDF pretreatment by ionic liquid were as follows: preparation for 194.31 min at 143.08 °C with a solid–liquid ratio of 1:20 and ionic liquid concentration of 18.65%. Under the optimized conditions, the maximum concentration of FOs was predicted to be 0.943 mol/L. To verify the validity and reliability of the model, the concentration of FOs in the repeated validation test was 0.906 mol/L. Combined with the total content of FA in IDF, the yield of FOs increased from 48.6 ± 0.02% to 74.76 ± 0.03%, which is as 1.5 times high as compared with that from untreated IDF.

Effect of ILs on the physical and chemical properties of corn bran IDF

Fig. 3A shows the FT-IR spectrum of corn bran insoluble dietary fiber after pretreatment (400 ~ 4 000 cm^{-1}), which provide information about the chemical composition, molecular conformation and hydrogen bond properties of dietary fiber (Caputo et al., 2021). As indicated by the characteristic signal peaks, no new functional groups and derivatives appeared after the ILs pretreatment. O—H stretching bands of cellulose and hemicellulose appeared at 3400 cm^{-1}. The absorption peaks approximately 2918 cm^{-1} are the stretching vibrations of saccharide methyl and methylene C—H. The absorption peak at 1735 cm^{-1} was
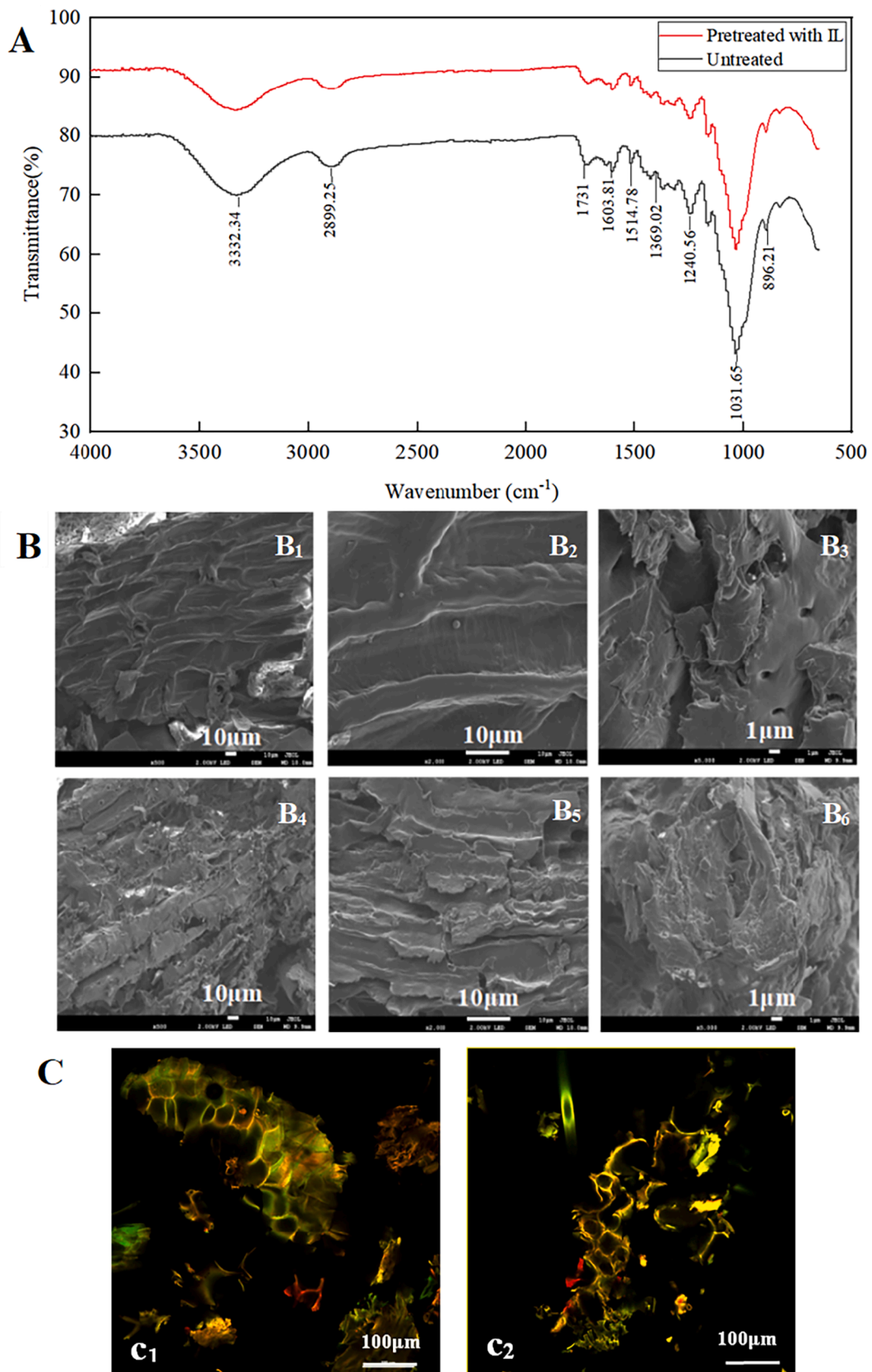
Fig. 3. (A) FTIR of IDF before and after treatment of IL, (B)Scanning electron microscope of IDF untreated and pretreated with IL, (C)Confocal micrographs of IDF untreated and pretreated with IL.

derived from the sugar ester bond group. The result was consistent with previous study (Hu et al., 2018), in which the basic skeleton structure of hemicellulose does not disappear after IL pretreatment. On the other hand, 1513 cm^{-1}, 1603 cm^{-1}, 1369.02 cm^{-1}, 1240 cm^{-1}, and 1050 cm^{-1} correspond to the acetyl stretching vibration of lignin, the C=C of the aromatic ring of lignin, the C—H vibration of hemicellulose and cellulose, the C—O in the aromatic ring, and the stretching vibration and C-OH bending of hemicellulose, respectively, all of which were significantly weakened. In addition, the absorption peak of the β-glycosidic bond between the amorphous cellulose and hemicellulose main chain that appeared at 898 cm^{-1} was weakened (Aa, Naaj, & Isa, 2022). The changes in the above characteristic peaks can be simply understood as the formation of new chemical bonds with the components of IDF cellulose using the anion of IL as the electron donor and the cation as the electron acceptor to weaken the interchain and intrachain hydrogen bonds of cellulose and hemicellulose. The partial delignification of IDF makes the structure of IDF loose, delignification occurs (Mastura Zakaria, Azila, Kumuthini, & Yatimah, 2020), and the adsorption capacity is enhanced. Notably, the regenerated hemicellulose has more uniform structural characteristics and lower thermal stability, which can explain the resulting improvement of the enzymatic hydrolysis efficiency (Xia et al., 2020).

Additionally, the tight structure of lignocellulose is one of the reasons for the low enzymatic hydrolysis efficiency. The surface morphology of the IDF observed by SEM (500×, 2000× and 5000×) was shown in Fig. 3B. The surfaces of cellulose and hemicellulose were tightly wrapped but with little exposure and no obvious fracture by lignin in the raw material. After pretreatment, cracks appeared in the original rigid structure, which showed dense cross-linking structures among cellulose, hemicellulose and lignin and became porous and loose. By increasing the surface area of hemicellulose, more enzyme binding sites are available for hydrolysis. As previously speculated, IL breaks van der Waals forces and hydrogen bonds by forming new chemical bonds with lignin, cellulose and hemicellulose (He et al., 2021).

The changes in the phenolic substance content and IDF microstructure were further observed by CLSM. The microstructure of the IDF was visualized by staining with Congo red, which showed green fluorescence. The red color is caused by the auto-fluorescence of phenolic substances, especially the high content of ferulic acid, which binds to dietary fiber (Wallecan, McCrae, Debon, Dong, & Mazoyer, 2015). The combined Fig. 3C indicates that the unprocessed overall structure is more complete than that pretreated one without being disintegrated. The rigid connection structure of IDF is more dispersed after pretreatment. Compared with Fig. 3C1, the red fluorescence signal was significantly enhanced in Fig. 3C2, indicating that more phenolic acids were exposed. Overall, it was beneficial to reduce the resistance of subsequent enzymatic hydrolysis of IDF and improve accessibility.

To sum up, the possible mechanism of imidazole carboxylic acid-type IL applied for the pretreatment of corn bran IDF is shown in Fig. 4. The cationic acid C2-H proton of the imidazole carboxylate ILs forms hydrogen bonds with the ether and bridge oxygen atoms in the hemicellulosic molecules, and the carboxylate anion forms hydrogen bonds with OH protons in hemicelluloses (Yuan et al., 2019). The effect of water in the pretreatment system is to reduce the viscosity of [Amim]OAc, improve the diffusion coefficient of [Amim]OAc in the pretreatment process, so as to enhance the diffusion performance.

After four cycles of IL, FOs concentration increased by 49.75%, 45.58%, 32.73%, 25.15%, proving that the pretreatment performance of IL did not disappear after four cycles of IL, it can be recycled and cost saving. However, recycled IL contains more water, the recycled IL water content can not only be reduced by rotary evaporation, resulting in inaccurate quantitative of concentration. In the recycling process, the amount of IL itself after dissolution, the number of IL washes is not enough. The accumulated polysaccharide lignin impurities bond with part of IL and saturate it, which also leads to the decrease of the pretreatment effect of IL. Further cost savings can be achieved if the recycling steps can be optimized later.

Conclusion

In this study, the optimal IL ([Amim]Ac corn bran IDF pretreatment for enzymatic-assisted extraction of FOs from corn bran IDF) was obtained. The pretreatment parameters were optimized by a single factor test and response surface methodology. The concentration of FOs was 0.906 mol/L after treatment for 194.31 min with an ionic liquid concentration of 18.65% at 143.08 °C. The FOs extraction yield was as 1.5 times high as compared with the conventional enzymatic-assisted extraction. The ionic liquid pretreatment was proved to be a feasible method to loosen the dense cross-linking structures among cellulose, hemicellulose and lignin. However, the pretreatment of IL with optimal condition will not affect the basic skeleton structure of hemicellulose. In addition, the recycled IL was also effective to loosen the dense cross-linking structures among cellulose, hemicellulose and lignin after 4 times of recycles. With the excellent recyclability of ionic liquids, research on environmentally friendly and efficient preparation of natural products will be more mature and in-depth in the future. In summary, the present study resulted in a more effective approach for obtaining a natural soluble conjugated-phenolic from plant fibers. In addition, the whole process represents a promising contribution to designating a new destination to food wastes.
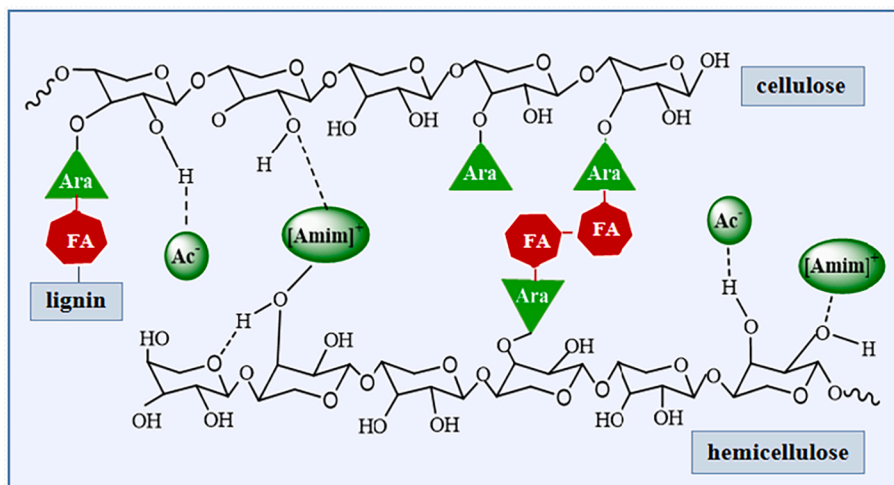

Fig. 4. Diagram of possible mechanisms in the preprocessing process (Ara-arabinose, FA-Ferulic acid).

CRediT authorship contribution statement

Lingxiao Gong: Conceptualization, Methodology, Supervision, Writing – review & editing. **Dannin Feng:** Data curation, Investigation, Writing – original draft. **Jie Liu:** Supervision, Validation. **Yonghui Yu:** Formal analysis, Writing – review & editing. **Jing Wang:** Funding acquisition, Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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