

Preparation and optimization of macroalgae-derived solid acid catalysts

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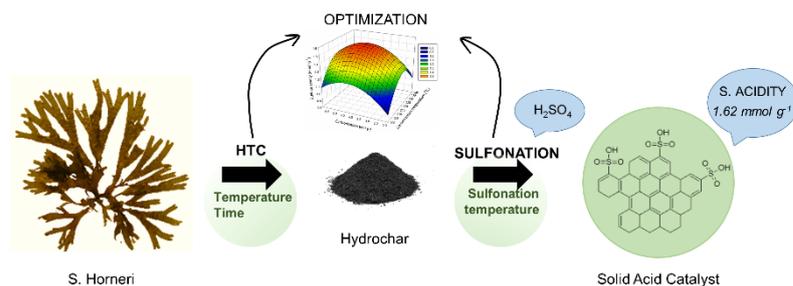
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Abstract

Solid acid catalysts were synthesized from macroalgae *Sargassum horneri* via hydrothermal carbonization followed by sulfuric acid sulfonation. A three-variable Box-Behnken design and optimization was used to maximize surface acidity. The optimal preparation conditions were found to be at the carbonization temperature of 217 °C, the carbonization time of 4.6 hours and the sulfonation temperature of 108.5 °C. Under these conditions, the highest surface acidity achieved was 1.62 mmol g⁻¹. Physical and chemical properties of prepared solid acid catalyst were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. The results proved the grafting of -SO₃H groups on an amorphous carbon structure. The catalyst activity was evaluated by the esterification of oleic acid with methanol. The sample prepared achieved 96.6% esterification yield, which was higher than the 86.7% yield achieved by commercial Ambersyst-15 under the same reaction conditions.

Graphical abstract



Keywords

Solid acid catalyst, biomass, hydrothermal carbonization, esterification, Box-Behnken design

1 Introduction

Solid acid catalyst (SACs) are a group of widely used heterogeneous catalysts for a variety of industrial reactions. Compared to conventional liquid acid catalysts, SACs are non-corrosive, environmentally benign and present fewer separation and disposal problems.[1, 2] The types of SACs available include zeolites, metal oxides, ion-exchange resins, phosphates and carbonaceous materials. Recently there has been great interest in the synthesis of SACs using carbonaceous materials derived from biomass as support. A variety of biomass has been investigated, including pelletized peanut hulls, pine pellets and pine chip char[3], rice husk[4], corn straw[5], corncob[6], cassava stillage[7] bagasse[8], oil palm trunk[9], and microalgae residue[10].

Most of the biomass derived SACs are synthesized by a two-step method, e.g. a carbonization step followed by a sulfonation step. Kastner *et al.*[3] prepared a carbon support by pyrolysis of wood at 400-500 °C and the $-SO_3H$ groups were then introduced by reacting the carbon support with concentrated H_2SO_4 or SO_3 gas. The same pyrolysis-sulfonation method has been applied to rice husk[4], corn straw[5], cassava stillage[7], bagasse[8] and oil palm trunk[9]. Another two-step route is the hydrothermal carbonization-sulfonation method, which was claimed to be less energy intensive than the pyrolysis-sulfonation route. Ma *et al.*[6] prepared hydrochars by hydrothermal carbonization of corncob at 120-240 °C. The hydrochars were reacted with concentrated H_2SO_4 at 60-150 °C to obtain

SACs. Magnetic SACs were prepared using the same route from banana peel feedstock.[11] Apart from the two-step method, one-step synthesis of SACs from biomass was also reported in the literature. SAC was synthesized by in situ partial carbonization and sulfonation of microalgae residue with sulfuric acid at 180 °C.[10]

As biomass derived SAC is a relatively new research area, there is limited information on the optimization of the synthesis process. Recent years, response surface methodology (RSM) has been widely used to optimize chemical and biochemical engineering processes. RSM is a combination of mathematical and statistical techniques which can be used to evaluate the importance of process variables and improve processes. [12] Design methods such as central composite design (CCD) have been used to optimize the synthesis of ZnS:Cu nanoparticles on activated carbon [13] and pectin extraction from banana peels [14]. Compared to CCD, another RMS-based method, Box-Behnken design, has the advantages of a reduction in the number of experiments and no experiments are performed under extreme conditions. [15] It has been successfully applied for the optimization of various processes, such as solvent extraction [16, 17], adsorption [18, 19], and material synthesis [20, 21].

Our previous work successfully prepared hydrochar from *Sargassum horneri* (*S. horneri*) via the hydrothermal carbonization process. [22] The principal objective of the present work was to investigate the feasibility of using the same macroalgae as a feedstock for the production of solid acid catalyst via hydrothermal carbonization and sulfonation. The prepared solid acid catalysts were characterized using various analytical methods. The catalytic activity was evaluated by the esterification of oleic acid with methanol. The second objective was to study the effects of the synthesis conditions on surface acidity. The Box-Behnken design was applied to optimize the synthesis conditions and maximize surface acidity of prepared solid acid catalysts. It was the first time that the production of solid acid catalysts from macroalgae was investigated and optimized. The work also demonstrated that the importance of the synthesis conditions and their interaction, which would assist further scale-up of the process.

2 Material and methods

2.1 Raw material and pre-treatment

Adult male and female *S. horneri* plants were sampled from the rocky shore at the intertidal zones on the Nanji Islands (27.4634° N, 121.0796° E), Wenzhou City, China. The composition of the raw *S. horneri* sample is listed in Table 1. After sampling, the plants were air-dried and delivered to the laboratory. For this study, the raw material was washed with de-ionized water, dried for 6 hours, ground and sieved through a MESH 30 sieve. The powders were dried at 110 °C until a stable mass was reached, and then stored in a desiccator for further use.

Concentrated sulfuric acid (98%), sodium chloride, sodium hydroxide, oleic acid and anhydrous methanol was purchased from Sinopharm (China) and used as received.

2.2 Hydrothermal carbonization

The hydrothermal carbonization process was conducted in a non-stirred 100 mL para-polyphenylene (PPL)-lined stainless steel autoclave (KH-100 ml, Shanghai Lingke Ltd., China). A total of 5 g of dried *S. horneri* powder and 50 ml de-ionized water was added to the autoclave. The autoclave was sealed and transferred to a preheated oven (DHG-9021A, Hangzhou Lantian, China) at required temperature. After the reaction, the autoclave was cooled to room temperature. The solid product was filtered, washed with de-ionized water, and finally dried at 110 °C until a stable mass was reached. The dried solid product, hydrochar (HTC), was stored in a desiccator for further treatment and characterization.

2.3 Sulfonation

A known amount of concentrated sulfuric acid (98%) and 2 g of the hydrochar sample were mixed in a flask and heated at 50-130 °C for 1-8 hours. After cooling to room temperature, the mixture was diluted with 500 mL de-ionized water and stirred overnight. The product was filtered and thoroughly washed with de-ionized water until a pH of 7 was achieved. The material was then dried at 110 °C and stored for further characterization.

2.4 Optimization of synthesis process

In the synthesis process, there are various parameters that have an effect on the surface acidity and thus catalyst activity. The conventional approach of experimenting with one variable at a time is time-consuming and labour intensive. The Box-Behnken experimental design method, one of the response surface methodologies, was used to find the optimum synthesis conditions to achieve highest surface

acidity. The Box-Behnken design was chosen over the usual central composite design as it has the advantage to avoid treatment combinations that are extreme. The combinations of extreme temperatures and long exposure times during the HTC process could lead into the break of the carbonaceous structure and therefore loss of data. Before applying the Box-Behnken experimental design, a series of single variable experiments were carried out to identify the key experimental variables and their examinable ranges.

2.5 Single variable experiments

Five variables were chosen for the single variable experiments. They include the carbonization temperature, the carbonization time, the sulfonation temperature, the sulfonation time and the amount of H₂SO₄ added during the sulfonation. The ranges of the variables were selected according to literature [6]. The reaction conditions for the single variable experiments are listed in Table 2. For each variable investigated, the other variables were kept at the base conditions, which are listed in bold type in Table 2.

2.6 Box-Behnken design

The single variable experiments showed that the carbonization temperature, the carbonization time, and the sulfonation temperature were the key variables. The examinable ranges for the three variables were determined as 200-240 °C, 2-6 hours and 70-110 °C, respectively. In order to find the optimum synthesis conditions to achieve highest surface acidity, a Box-Behnken experimental design with 3 variables, 3 levels and 17 runs was applied. The number of experiments was determined according to:

$$N = k^2 + k + c_p \quad (1)$$

where k is the variable number and c_p is the replicate number of the central point. The three levels were coded as -1 (low), 0 (middle) and 1 (high). Table 3 provides the variables and levels of the Box-Behnken design.

Obtained values for response variable (Y) could be approximated by a quadratic polynomial model according to the input variables X₁, X₂ and X₃:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where β_0 is the offset term, β_i is the linear slope and β_{ii} reflects the quadratic effect, both for variable X_i , β_{ij} represents the interaction between X_i and X_j and finally ε is a random error.[23]

The influence and significance of independent variables and the importance of their interactions were analysed using ANOVA (Analysis of Variance). Results were evaluated using statistical parameters such as degrees of freedom, p-values and F-values and determination coefficient (R^2) to assess the statistical significance of the quadratic model. Design-Expert v8.0 was used for the Box-Behnken design and data analysis.

2.7 Characterizations

FT-IR spectra were collected in the range of 400–4000 cm^{-1} using a potassium bromide palletization method on a Thermo-Nicolet Nexus 670 FT-IR spectrometer. A total of 64 scans were taken for each interferogram at 4 cm^{-1} resolution. Elemental analysis (C, H, N, and S) of the samples was carried out on a vario MACRO cube analyzer. Oxygen content was determined by difference. X-ray diffraction analysis (XRD) was conducted on a PANalytical X'Pert Pro diffractometer.

2.8 Surface acidity analysis

The surface acidity was measured by acid-base titration. 0.05 g sample and 15 mL 2 M NaCl were placed in a 50 mL conical flask. The mixture was mixed in an ultrasonic bath for 30 mins to accelerate the ion-exchange. The mixture was filtered, and the filtrate was then titrated using 0.05 M NaOH aqueous solution. The surface acidity was calculated by the amount of NaOH solution consumed.

2.9 Catalytic activity analysis

The catalytic activity of the prepared samples was measured by esterification of oleic acid and methanol.[5] The esterification was carried out in a 100 mL three-necked flask with a magnetic stirrer and a condenser. For a typical run, the oleic acid and the catalyst were added to the reactor, followed by the introduction of methanol at the required temperature. The esterification yield was calculated by the change of the acid values before and after the reaction.

$$\text{Esterification yield (\%)} = \frac{AV_0 - AV_1}{AV_0} \times 100 \quad (3)$$

where AV_0 and AV_1 are the acid values before and after the reaction, respectively.

The acid value is defined as the weight of KOH in mg needed to neutralize the organic acids present in 1 g of oil. The method presented in the Chinese Standard GB/T5530-2005 was used to determine the acid values.

3 Results and discussion

3.1 Single variable experiments

The effects of the five selected variables on the surface acidity were investigated by a series of single variable experiments in which only one variable was changed at a time.

The effect of the carbonization temperature on the surface acidity was investigated by varying the carbonization temperature from 180 to 260 °C. The results are shown in Fig. S1a. The surface acidity increased from 0.8 mmol g⁻¹ to over 1.4 mmol g⁻¹ when the carbonization temperature was increased from 180 to 220 °C. However, further increasing the temperature caused a reduction in the surface acidity. At the lower temperature of 180 °C, the degree of carbonization was low. Therefore the product was not suitable as a support for solid acid catalyst. With increasing carbonization temperature, further carbonization occurred and more active aromatic carbons were formed, which prefer sulfonation. The maximum value reached at 220 °C may be due to the formation of amorphous carbon composed of small aromatic carbon sheets, to which -SO₃H group can be easily bonded. However, excessive higher temperature resulted in the opposite effect on the surface acidity. Carbonization time has a similar explanation and effect on surface acidity, as shown in Fig. S1b.

Optimal sulfonation conditions was found to vary for the different materials. As can be seen in Fig. S1c, surface acidity increases from 0.6 mmol g⁻¹ to 1.46 mmol g⁻¹ at 90 °C and then decreased. The results obtained match other similar studies. For example, the preparation of solid acid catalyst from rice husk char[4], in which the best sulfonation temperature was also 90 °C and the catalyst showed an oleic acid conversion of 98.7% obtaining a sulfonated product with excellent stability.

The effect of the sulfonation time on the surface acidity is shown in Fig. S1d. The surface acidity was low when the sulfonation time was 1 hour. This indicates that the sulfonation reaction was not complete after 1 hour. When the sulfonation time was longer than 2 hours, it had little effect on the surface acidity,

indicating that the sulfonation reaction was finished after 2 hours. Therefore no optimization was investigated further for this parameter. The sulfonation time was set as 2 hours for further experiments.

The effect of the amount of sulfuric acid added on the surface acidity is shown in Fig. S1e. When less than 15 mL sulfuric acid was added, the sulfonation reaction was not complete, resulting in a lower surface acidity. It has little effect on the surface acidity when the amount of sulfuric acid added was more than 15 mL. No further optimization was carried out on this variable. The amount of sulfuric acid added was set as 15 mL for further experiments.

The preliminary single variable experiments showed that the carbonization temperature, the carbonization time and the sulfonation temperature were the key variables to achieve the highest surface acidity. These three variables were selected for further optimization using the Box-Behnken design.

3.2 Box-Behnken design

Independent variables and their values for the Box-Behnken design used in the study are shown in Table 4. The experiment at the central point was repeated five times. The mean surface acidity under the condition was $1.546 \pm 0.011 \text{ mmol g}^{-1}$, indicating a good reproducibility of the process.

According to the results, the response, surface acidity (Y), can be expressed as a quadratic regression model of carbonization temperature (T_c), carbonization time (t_c) and sulfonation temperature (T_s):

$$Y = 1.55 + 0.046X_1 + 0.075X_2 + 0.18X_3 - 0.015X_1X_2 - 0.15X_1X_3 + 0.046X_2X_3 - 0.31X_1^2 - 0.21X_2^2 - 0.12X_3^2 \quad (3)$$

where

$$X_1 = \frac{T_c - 220}{20}$$

$$X_2 = \frac{t_c - 4}{2}$$

$$X_3 = \frac{T_s - 90}{20}.$$

Coefficients of the model were assessed by regression analysis. Statistical analysis revealed whether it was necessary to exclude insignificant coefficients from the model. The model-fitted values of the surface acidity were calculated from Equation (3) and listed in Table 4.

The ANOVA of the quadratic regression model is shown in Table 5. The model had an F-value of 42.58 and a p-value less than 0.0001, which indicated that the model was significant and properly fitted to the response data. The value of the determination coefficient ($R^2=0.9821$) indicated that the model can explain 98.21% of the variation in the surface acidity.

The p-values of the independent variable, sulfonation temperature (X_3), the quadratic term of the carbonization temperature (X_1^2) and the quadratic term of carbonization time (X_2^2) were all lower than 0.0001, showing that they were the most significant variables in the quadratic expression and had the largest influence on the surface acidity.

The percentage of contribution for each individual term was calculated by the ratio of adjusted sum of squares of each term to the total sum of squares. The results are shown in Table 5. Among all the terms considered, the quadratic term of the carbonization temperature (X_1^2) was the most influential with in the model, accounting for 35.7%; followed by the sulfonation temperature (X_3 , 23.5%) and the quadratic term of the carbonization time (X_2^2 , 15.7%).

Additionally, the interaction existing between the carbonization temperature and the sulfonation temperature (X_1X_3) with a p-value of 0.0008 and a percentage of contribution of 8.0% shows a weaker influence but still significant in the response. Other interactions like the carbonization time and temperature (X_1X_2) showed the lowest effect on the surface acidity.

In order to gain a better understanding of the effects of the interactions between two variables on the surface acidity, the model was presented in Figs 2-4 as two-dimensional contour plots and three-dimensional response surface curves.

Fig. 1 represents the interaction between the carbonization temperature (X_1) and the carbonization time (X_2) when the sulfonation temperature was 90 °C. The contour lines were circular, indicating that the interactions between the carbonization temperature and carbonization time were negligible. The maximum surface acidity that could be achieved was 1.554 mmol g⁻¹ when the sulfonation temperature was 90 °C.

Fig. 2 shows the combined effect of the carbonization temperature and the sulfonation temperature on the surface acidity at a constant carbonization time of 4 hours. The highest surface acidity achieved

was 1.6 mmol g⁻¹. Oval contour lines indicated a better correlation between the mentioned variables than the ones in Fig. 1 where the lines were circular. That fact was consistent with the p-values for X₁X₃ interaction and X₁X₂ interaction obtained in ANOVA.

Fig. 3 shows the interactive influence of the carbonization time and the sulfonation temperature when carbonization temperature was fixed at 220°C. For the 3D response surface plot and the studied range for the sulfonation temperature, the surface acidity was clearly increasing while the sulfonation temperature increased. In terms of the carbonization time, a parabolic trend was observed. The highest value achieved was 1.62 mmol g⁻¹. The 2D contours indicated a weak interaction between the studied variables.

3.3 Validation of the model

According to the model, the predicted maximum surface acidity was 1.638 mmol g⁻¹ when the carbonization temperature is 217.0 °C, the carbonization time is 4.6 hours and the sulfonation temperature is 108.0 °C. In order to validate the adequacy of the model, three experiments were carried out at the predicted optimum condition. The average surface acidity obtained in the three validation experiments was 1.615 mmol g⁻¹, which was in good agreement with the predicted maximum, with an error of 1.4%. The validation result indicated that the model developed by the Box-Behnken was accurate.

3.4 Characterizations of the prepared solid acid catalysts

The hydrochar and sulfonated hydrochar prepared at the optimum condition were named as HTC and HTC-S. The two samples and the raw *S. horneri* were characterized by various technologies, including elemental analysis, FT-IR and XRD, in order to understand their physical and chemical properties.

The results from the elemental analysis of raw *S. horneri*, hydrochar (HTC) and sulfonated hydrochar (HTC-S) are listed in Table 6. After hydrothermal carbonization, the carbon content increased while hydrogen and oxygen contents reduced as expected. The sulphur content remained unchanged. After sulfonation, the sulphur and oxygen contents increased from 1.0% to 5.4% and 41.0% to 46.8%, respectively. It indicated that the –SO₃H groups were successfully introduced on the hydrochar through sulfonation procedure.

The FT-IR spectra of hydrochar and sulfonated hydrochar were used to examine the surface functional groups. The FT-IR spectra of the samples are illustrated in Fig. 4. Both HTC and HTC-s had a broad absorption band at 3000-3600 cm^{-1} , attributed to OH stretching vibration in the hydroxyl or carboxyl groups. However, the centre of the band was shifted from 3341 cm^{-1} for the hydrochar to 3402 cm^{-1} for the sulfonated sample. The same phenomena was observed by Ma *et al.*[6]

The hydrochar had stronger absorption bands at 3000-2800 cm^{-1} , which attributes to stretching vibrations of aliphatic C-H. After sulfonation, the strength of the peaks reduced, while the peak at 3010 cm^{-1} became more visible which is attributed to C-H vibration of the aromatic ring. It indicated that aliphatic hydrocarbon was converted into aromatic compounds during the sulfonated process. New peaks assigned to O=S=O symmetric stretching and SO_3 stretching modes appeared at 1025 and 1152 cm^{-1} . It further indicates that SO_3H groups were introduced onto the hydrochars.

The PXRD patterns for the HTC and HTC-S samples are shown in Fig. 5. Both HTC and HTC-S had a broad (002) diffraction peak at the 2θ of 23°, which is attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.[24] After sulfonation, the (002) peak became sharper and moved from 22.76° to 23.05°. The observation suggested that the carbon structure became more organized due to the sulfonation. In the PXRD pattern for HTC-S, the peaks for CaSO_4 crystals were observed. It was due to high concentration of calcium ions presented in macro-algae.

3.5 Performance of solid acid catalyst

The catalytic activity of the prepared solid acid catalyst was first tested by the esterification of oleic acid and methanol. At 90 °C and 2.7 hours, the reaction achieved 96.6% esterification yield using HTC-S. For comparison, Amberlyst-15 was used as the benchmark. At the same reaction conditions, the reaction achieved a yield of 86.7% using Amberlyst-15. It shown that the biomass based HTC-S had higher activity for esterification of oleic acid and methanol than Amberlyst-15.

The solid acid catalyst was also tested for its ability to be reused. The catalyst was separated from the reaction medium, washed, dried and then reused. The esterification yield reduced from 96.6% to 85.1% after being reused 7 times (Fig. 6). The surface acidity was reduced after each use, from 1.62 to 0.82 mmol g^{-1} . It indicated that part of the surface acid groups are soluble in solvent.

4 Conclusions

The optimal preparation condition of Sargassum Horneri derived solid acid catalyst were at a carbonization temperature of 217 °C, carbonization time of 4.6 hours, concentrated sulfuric acid volume of 15 mL, the sulfonation temperature of 108.5 °C and sulfonation time of 2 hours. Under this condition, the surface acidity measured by experiment could reach 1.62 mmol g⁻¹.

The results of crystal structure analysis, elemental analysis and surface functional group analysis indicated that the sulfonic acid group was successfully loaded onto the surface of an amorphous carbon structure. The catalyst activity test showed that the macroalgae derived solid acid catalysts had high catalyst activity.

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List of tables and figures

Table 1 Elemental analysis, proximate analysis and biochemical content of raw *S. horneri* sample.

Table 2 Experimental conditions for single variable experiments. The bold numbers are the base case condition.

Table 3 Experimental variables and levels in Box-Behnken design

Table 4 Box-Behnken runs with actual values for the three independent variables and the experimental and model-fitted responses

Table 5 Results of ANOVA for the surface acidity

Table 6 Elemental analysis of *S. horneri*, hydrochar (HTC) and sulfonated hydrochar (HTC-S).

Fig. 1 Response surface and contour plots for the effects of the carbonation time and the carbonation temperature on the surface acidity

Fig. 2 Response surface and contour plots for the effects of the carbonation temperature and the sulfonation temperature on the surface acidity

Fig. 3 Response surface and contour plots for the effects of the carbonation time and the carbonation temperature on the surface acidity

Fig. 4 FT-IR spectra of hydrochar (HTC) and sulfonated hydrochar (HTC-S)

Fig. 5 PXRD patterns of hydrochar (HTC) and sulfonated hydrochar (HTC-S). ■ amorphous carbon, ▲ CaSO₄.

Fig. 6 Reusability of the HTC-S prepared under the optimized conditions.

Table 1 Elemental analysis, proximate analysis and biochemical content of raw *S. horneri* sample.

	Content (% dry basis, \pm standard deviation)
Elemental analysis	
Carbon	35.3 \pm 0.3
Hydrogen	5.7 \pm 0.3
Oxygen	56.3 \pm 0.9
Nitrogen	1.7 \pm 0.2
Sulfur	1.0 \pm 0.1
Proximate analysis	
Moisture	5.5 \pm 0.4
Volatile matter	61.2 \pm 5.3
Fixed carbon	21.2 \pm 1.8
Ash	12.1 \pm 0.8
Biochemical content	
Cellulose	38 \pm 3.1
Hemicellulose	22 \pm 1.9
Lignin	22 \pm 3.0

Table 2 Experimental conditions for single variable experiments. The bold numbers are the base case condition.

Variable					
Carbonization temperature (°C)	180	200	220	240	260
Carbonization time (h)	1	2	4	6	8
Sulfonation temperature (°C)	50	70	90	110	130
Sulfonation time (h)	1	2	4	6	8
The amount of H ₂ SO ₄ added (mL)	5	10	15	20	25

Table 3 Experimental variables and levels in Box-Behnken design

Independent variables	Code	Level		
		-1	0	1
Carbonization temperature (°C)	X ₁	200	220	240
Carbonization time (h)	X ₂	2	4	6
Sulfonation temperature (°C)	X ₃	70	90	110

Table 4 Box-Behnken runs with actual values for the three independent variables and the experimental and model-fitted responses

Run No.	Carbonization temperature T_c ($^{\circ}\text{C}$)	Carbonization time t_c (hour)	Sulfonation temperature T_s ($^{\circ}\text{C}$)	Surface acidity Y , mmol g^{-1}	
				Experimental	Model-fitted
1	240	6	90	1.142	1.136
2	220	4	90	1.539	1.550
3	220	4	90	1.533	1.550
4	200	6	90	1.032	1.074
5	240	2	90	1.058	1.016
6	220	4	90	1.544	1.550
7	220	2	70	0.953	1.011
8	220	4	90	1.551	1.550
9	200	4	70	0.802	0.744
10	220	6	110	1.582	1.521
11	200	2	90	0.887	0.894
12	220	6	70	1.046	1.069
13	240	4	70	1.147	1.136
14	200	4	110	1.389	1.404
15	240	4	110	1.128	1.196
16	220	4	90	1.561	1.550
17	220	2	110	1.307	1.279

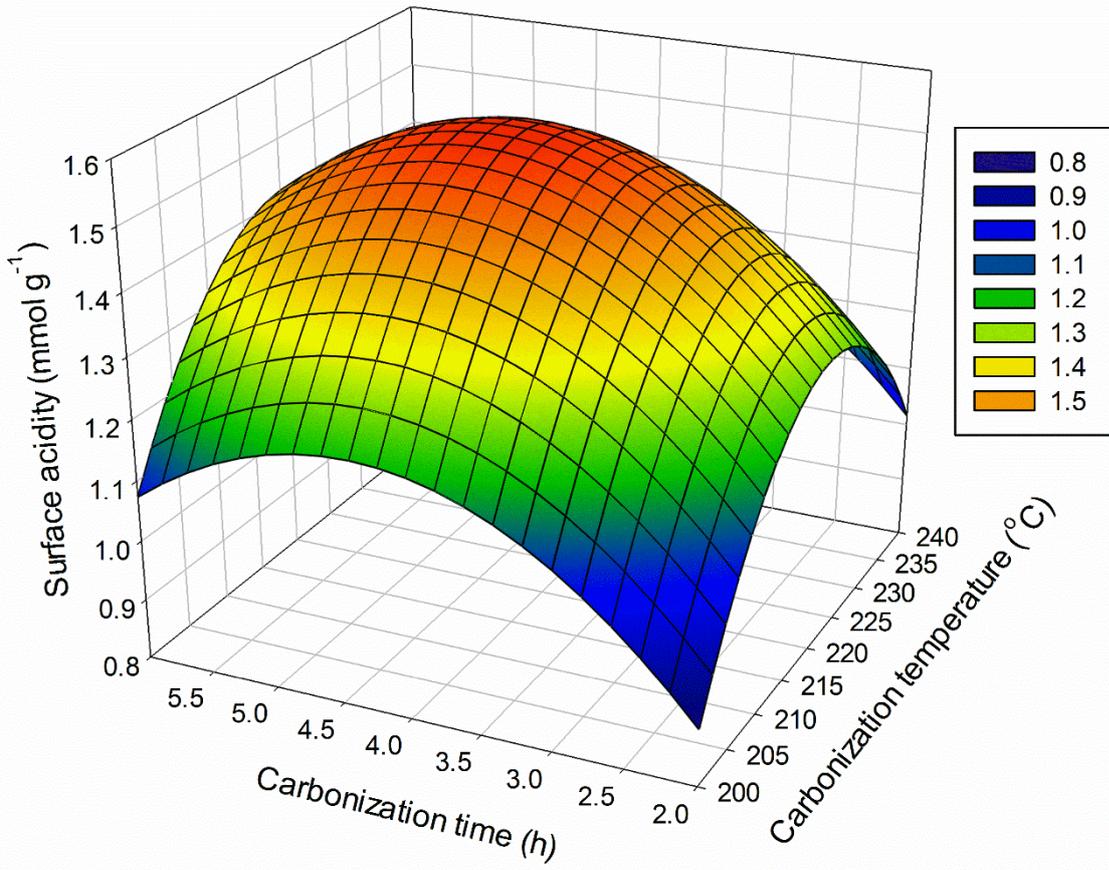
Table 5 Results of ANOVA for the surface acidity

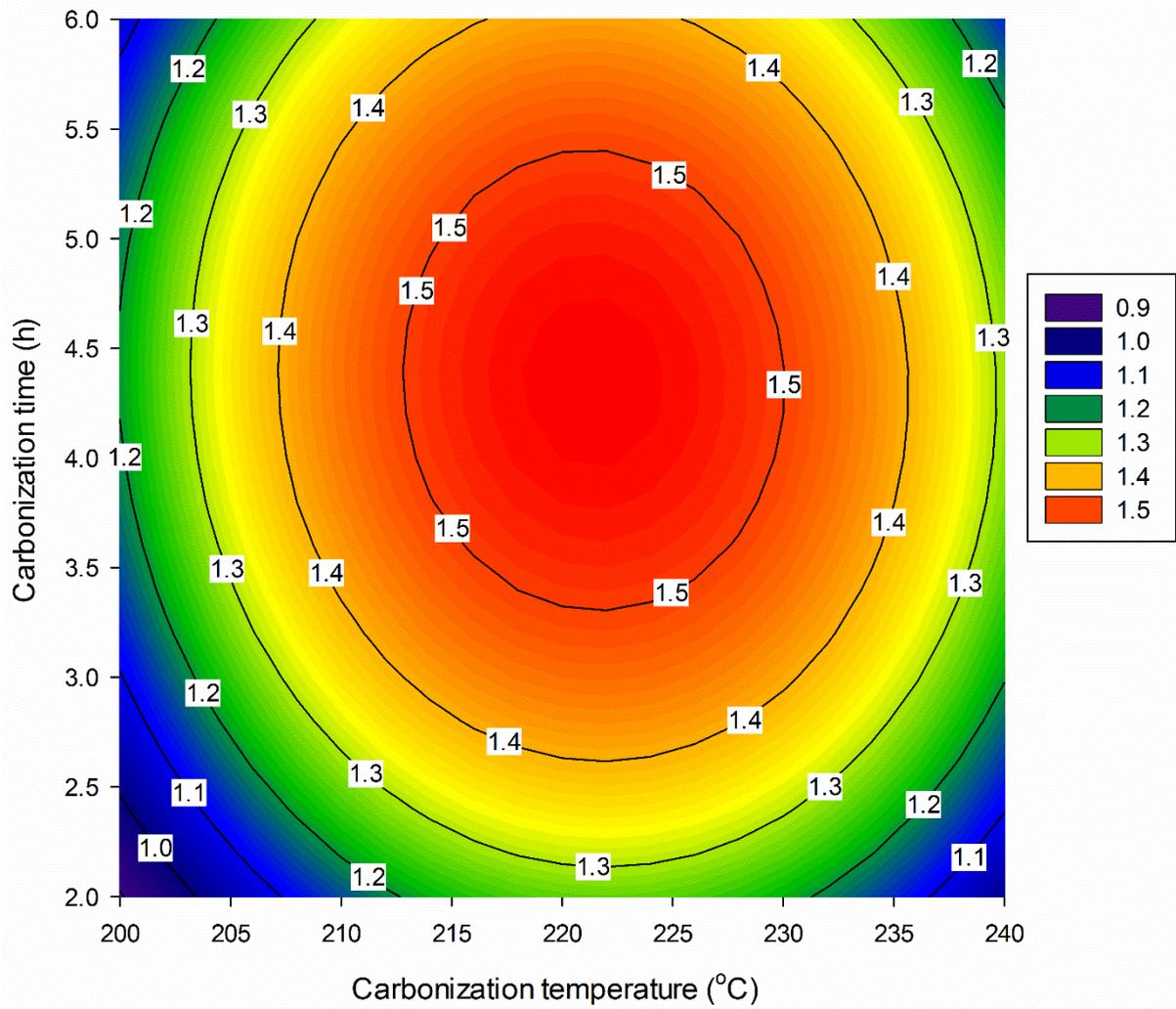
Source	Sum of squares	Degree of freedom	Mean square	F value	P value	Percentage of contribution	Significant ^a
Model	1.13	9	0.13	42.58	<0.0001		**
X ₁	0.017	1	0.017	5.63	0.0494	1.5%	*
X ₂	0.045	1	0.045	15.07	0.0060	3.9%	*
X ₃	0.27	1	0.27	89.87	<0.0001	23.5%	**
X ₁ X ₂	9.303×10 ⁻⁴	1	9.303×10 ⁻⁴	0.31	0.5924	0.1%	
X ₁ X ₃	0.092	1	0.092	31.05	0.0008	8.0%	*
X ₂ X ₃	8.281×10 ⁻³	1	8.281×10 ⁻³	2.80	0.1381	0.7%	
X ₁ ²	0.41	1	0.41	137.44	<0.0001	35.7%	**
X ₂ ²	0.18	1	0.18	59.95	0.0001	15.7%	**
X ₃ ²	0.059	1	0.059	19.97	0.0029	5.1%	*
Residual	0.021	7	2.957×10 ⁻³			1.8%	
R ²	0.9821						
Adjusted R ²	0.9590						

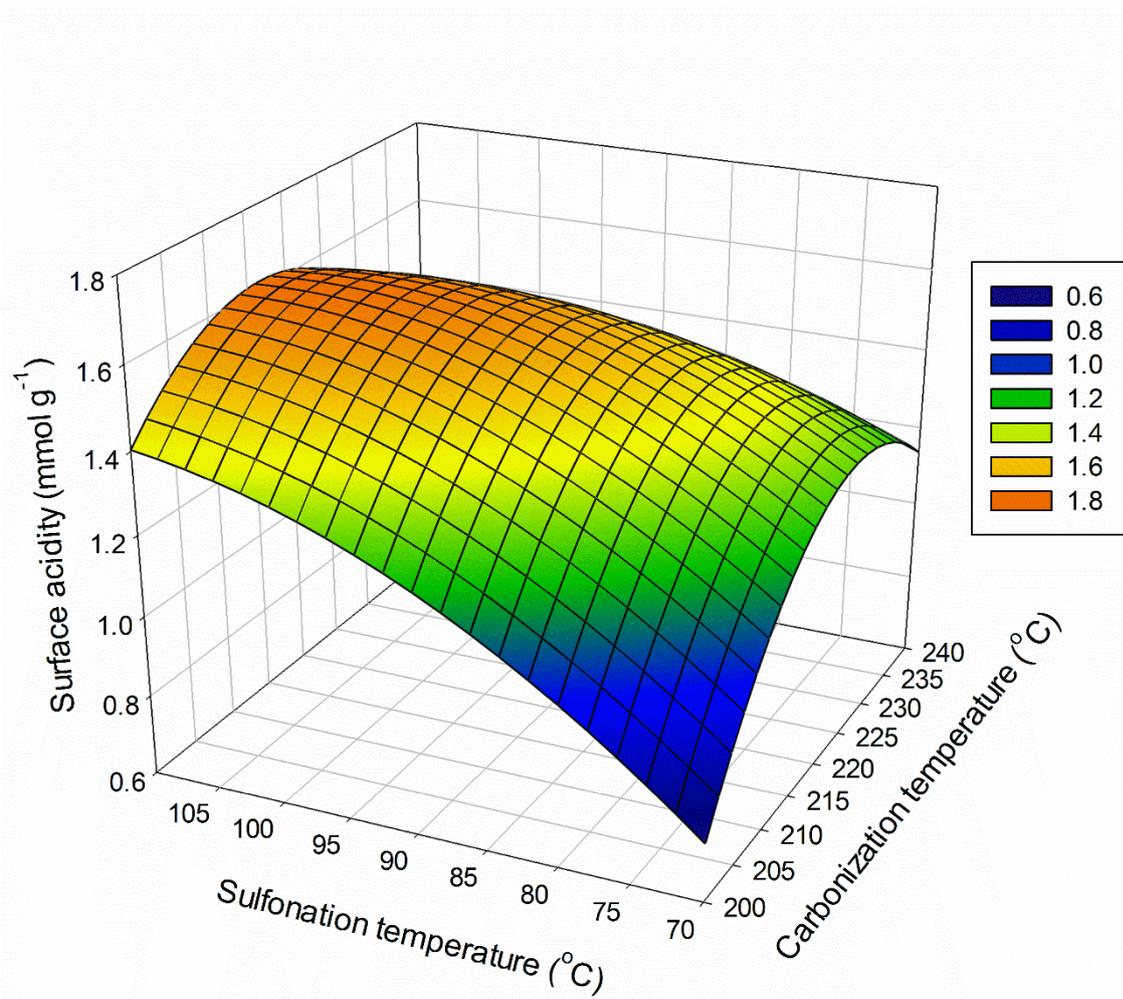
a. * p values ≤ 0.05 , ** p values ≤ 0.0001

Table 6 Elemental analysis of *S. horneri*, hydrochar (HTC) and sulfonated hydrochar (HTC-S).

Sample	Mass composition (%)					Chemical formula
	C	H	O	N	S	
<i>S. horneri</i>	35.3	5.7	56.3	1.7	1.0	$\text{CH}_{1.450}\text{O}_{0.894}\text{N}_{0.030}\text{S}_{0.008}$
HTC	50.9	4.9	41.0	2.2	1.0	$\text{CH}_{1.150}\text{O}_{0.604}\text{N}_{0.037}\text{S}_{0.007}$
HTC-S	42.3	4.0	46.8	1.5	5.4	$\text{CH}_{1.140}\text{O}_{0.830}\text{N}_{0.030}\text{S}_{0.048}$







Contour Graph 2

