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Evaluating the Application Potential of Acid-Modified Cotton Straw Biochars in Alkaline Soils Based on Entropy Weight TOPSIS

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Abstract: As a good carbon source and soil conditioner, biochar is widely used in acidic soils but seldom in alkaline soils due to its high pH. In this study, cotton straw biochar was modified with five different acidic materials to obtain wood-vinegar- (WBC), monosodium-glutamate (MSG)-wastewater- (MBC), citric-acid- (CBC), phosphoric-acid- (PBC), and nitric-acid-modified biochars (NBC), and three dosages were used for each modifier. The pristine and modified biochars were characterized with scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy. The biochar properties such as pH, specific surface area (SSA), and elemental contents were measured. In addition, the technique for order preference by similarity to ideal solution (TOPSIS) model based on entropy weight was used to evaluate the application potential of the biochars in alkaline soils. The FTIR spectra showed that modification with the five acidic materials, MSG wastewater in particular, resulted in more oxygen-containing functional groups such as O-H, C=O, and C-O on the biochar surface. In addition, acid modification greatly decreased the pH: phosphoric acid modification significantly decreased the pH of cotton straw biochar by 5.71–7.88 units. For the same modifier, a higher dosage (i.e., a smaller biochar:modifier ratio) led to a larger decrease in the pH of cotton straw biochar. The magnitudes of increase in total soluble salt content followed the general order of CBCs > PBCs > WBCs > NBCs > MBCs. The SSA, average pore diameter, and total pore volume of biochar were changed as well. Modification using wood vinegar and MSG wastewater significantly decreased the SSA of cotton straw biochar by 15.58–16.24 $m^2\ g^{-1}$ (82.7–86.2%) and 15.87–16.80 $m^2\ g^{-1}$ (84.2–89.2%), respectively, whereas modification using citric acid and nitric acid significantly increased the SSA of cotton straw biochar by 4.51–4.66 $m^2\ g^{-1}$ (23.9–24.7%) and 0.55–54.21 $m^2\ g^{-1}$ (2.9–287.7%). The evaluation based on entropy weight TOPSIS model suggested that the MBCs have the highest potential for application in alkaline soils. This study presents a theoretical basis for evaluation of biochar application potential, demonstrates a way of improving biochar application potential, and provides a support for beneficial utilization of agricultural and industrial wastes such as cotton straw, wood vinegar, and MSG wastewater.

Keywords: biochar; wood vinegar; monosodium glutamate wastewater; citric acid; phosphoric acid; nitric acid; alkaline soils; entropy weight TOPSIS

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1. Introduction

Today, land degradation is a worldwide concern. As low soil fertility limits agricultural production, it is very important to prevent land degradation [1]. Due to the arid climate, water stress is a common issue faced by agricultural production in northwest China. In addition, the soils are of low fertility, with low contents of soil organic matter, nitrogen (N), and phosphorus (P). These, together with land overuse, excessive chemical fertilizer application, and poor management, have led to soil salinization, posing a threat to agricultural production and ecosystem services [2–4]. As a vital approach to food security, soil restoration has recently attracted extensive attention from scientists and policy-makers [5].

Biochar is a black, carbon (C)-rich material prepared from biomass, such as wheat straw, maize straw, cotton straw, and tree branches, at temperatures ranging from 100 to 700 °C [6]. Although its physicochemical properties depend on the raw material, preparation temperature, and preparation method [7,8], biochar generally has a porous structure, a high specific surface area (SSA), and rich surface functional groups. Studies have shown that biochar application can improve soil structure, water and nutrient retention, and fertility [9,10], mitigate abiotic and biotic stresses (e.g., salinity, pollution, and pathogens) in plants [11], and reduce chemical fertilizer application without causing yield loss [12–19]. Biochar generally has a high pH and thereby is alkaline in nature. Therefore, it is commonly used in acidic and neutral soils and seldom applied in alkaline soils [20].

Biochar is often physically or chemically modified to extend its applicability [17,21]. It can be modified with acids to decrease its pH so that it can be applied to alkaline soils [22].

Compared to the pristine biochar, acid-modified biochar has more oxygen (O)-containing functional groups, a higher SSA, more pores, and a higher adsorption capacity [23]. Mahmoud et al. (2022) reported that the application of acid-modified rice straw and cotton straw biochars is an eco-friendly, cost-effective, and highly efficient approach to alleviating the adverse effects of saline–sodic stress on maize and wheat and increase their yields [24].

The beneficial effects of biochar on soil properties and agricultural production have been well documented [25–28]. Various methods have been used to evaluate the application potential of biochar, including gray correlation analysis [29,30], the factor analysis method [31], the fuzzy comprehensive evaluation method [20], and the technique for order preference by similarity to ideal solution (TOPSIS) model based on the entropy weight method [32]. Objectively reflecting the weight of each attribute is the key to ensuring the credibility of the evaluation results. The entropy weight method is a typical diversity-based weighting method, which calculates attribute weights based on the diversity of attribute data between alternatives [33]. Compared to the subjective assignment methods such as the hierarchical analysis method, the entropy weight method only involves simple calculation of objective data without subjective preferences [34]. The TOPSIS method has the advantages of simple logic, simple calculation, easy understanding, and considering the ideal solution and negative ideal solution at the same time. It is suitable for multi-attribute decision making with finite alternatives [35]. Therefore, the entropy weight TOPSIS method was used in this study to evaluate the agronomic application potential of 16 cotton straw biochars, comprising the pristine biochar and the 15 acid-modified ones. This study demonstrates the modification of cotton straw biochar with acids to enhance its applicability in alkaline soils and provides a support for the beneficial utilization of agricultural and industrial wastes such as cotton straw, wood vinegar, and monosodium glutamate (MSG) wastewater.

2. Materials and Methods

2.1. Reagents

Five acidic materials, namely, wood vinegar, MSG wastewater, citric acid, phosphoric acid, and nitric acid, were used for cotton straw biochar modification in this study. Basic information about them is given in Table 1. Wood vinegar, also called wood distillate, biooil, or pyroligneous acid, is a byproduct of biochar production from woody biomass. Due to the presence of organic acids such as acetic acid, formic acid, and propionic acid, wood vinegar

generally has a pH of 2–4. In addition, wood vinegar generally has high concentrations of N, P, and K. MSG wastewater, the N-rich wastewater from MSG production, has high concentrations of ammonium and sulfate and a very low pH (<4).

Table 1. The acidic materials used for biochar modification in this study.

Acidic Material	Purity or Main Ingredient Content	pH	Provider
Wood vinegar	Acetic acid 7–10%	2.92	Shijiazhuang Hongsen Activated Carbon Co., Ltd., Shijiazhuang, Hebei, China
Monosodium glutamate (MSG) wastewater	Ammonium sulfate 23–24%	3.67	Lotus MSG Factory, Fukang, Xinjiang, China
Citric acid	≥99.5%	1.30 (5% †), 1.10 (10%), 0.83 (20%)	Xinbute Chemical Co., Ltd., Tianjin, China
Phosphoric acid	≥85%	0.56 (10%), 0.32 (20%), 0.07 (30%)	Xinbute Chemical Co., Ltd., Tianjin, China
Nitric acid	36–38%	<0.01	Chengdu Cologne Chemical Co., Ltd., Chengdu, Sichuan, China

† Acid concentration.

All solutions were prepared with ultrapure water (18.2 MΩ cm, Millipore, Burlington, MA, USA). The chemicals and reagents used in the present study were of analytical grade.

2.2. Biochar Preparation and Modification

The cotton straw was collected from the Soil Improvement Experimental Station, Shihezi Reclamation Area, Xinjiang Uygur Autonomous Region, China. The cotton straw was air-dried, cut into 8–10 cm pieces, and pyrolyzed at 450 °C for 1 h in the absence of O_2 for biochar preparation. The prepared biochar was ground and sieved to <0.25 mm.

The biochar was then modified with wood vinegar, MSG wastewater, citric acid, phosphoric acid, and nitric acid to obtain wood-vinegar- (WBC), MSG-wastewater- (MBC), citric-acid- (CBC), phosphoric-acid- (PBC), and nitric-acid-modified biochars (NBC), respectively (Figure 1), according to the literature, with modifications [36–39]. Briefly, the cotton straw biochar powder was soaked in modifier solution for 24 h, with stirring every 8 h, and then oven-dried at 60 °C to constant weight. For each modifier, three dosages were used (Table 2). Therefore, a total of 15 modified biochars were prepared.

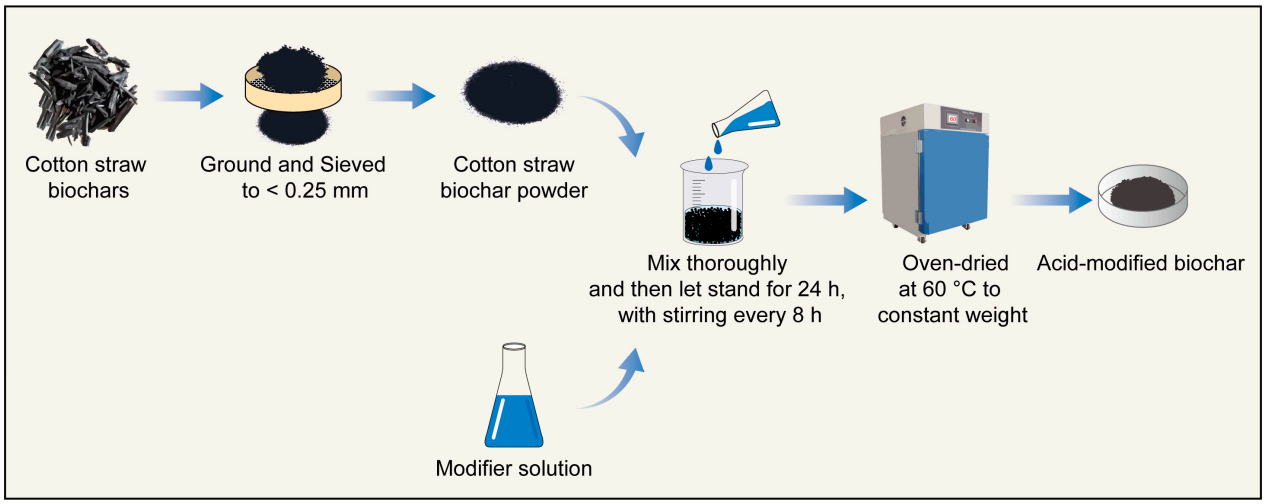


Figure 1. Flow chart showing the preparation of acid-modified cotton straw biochar.

2.3. Biochar Characterization

Biochar morphology was examined with a scanning electron microscope, small parts of the biochar specimen were selected. These specimens were subsequently gold-coated in a sputtering device and investigated using a scanning electron microscope (ZEISS Gemini SEM 500, USA) in the mode of secondary electrons (SE). The accelerating voltage was set to 2 kV.

Table 2. Biochar-to-modifier-solution ratios (i.e., modifier dosages) used for the preparation of acid-modified cotton straw biochars.

Biochar	Biochar-to-Modifier-Solution Ratio (W:V)	Abbreviation
Cotton straw biochar	-	BC
Wood-vinegar-modified cotton straw biochar (WBC)	1:0.8	WBC1
	1:1	WBC2
	1:1.5	WBC3
Monosodium-glutamate-wastewater-modified cotton straw biochar (MBC)	1:0.8	MBC1
	1:1	MBC2
	1:1.5	MBC3
Citric-acid-modified cotton straw biochar (CBC)	1:1 (5% †)	CBC1
	1:1 (10%)	CBC2
	1:1 (20%)	CBC3
Phosphoric-acid-modified cotton straw biochar (PBC)	1:1 (10%)	PBC1
	1:1 (20%)	PBC2
	1:1 (30%)	PBC3
Nitric-acid-modified cotton straw biochar (NBC)	1:1 (5%)	NBC1
	1:1 (10%)	NBC2
	1:1 (20%)	NBC3

† The concentration of the acid solution.

Surface functional groups were examined with Fourier-transform infrared (FTIR) spectroscopy (Thermo Scientific Nicolet iS5, Waltham, MA, USA), which was performed on cotton straw biochar beforehand. The cotton straw biochar sample and spectroscopy-grade KBr were dried at 105 °C for 4 h, and then, the sample was coground with KBr (1:100, wt/wt). The mixture was pressed into a pellet under infrared lamp exposure. The spectra were collected in the range of 4000 to 400 cm^{-1} at a step of 4 cm^{-1}.

A BEL SORP-max instrument was used for determination of SSA and pore size distribution. SSA was calculated using the Brunauer–Emmett–Teller (BET) method. Average pore diameter (APD) and total pore volume (TPV) were calculated using the Barrett–Joyner–Halenda (BJH) model.

pH was measured at a biochar:ultrapure water ratio of 1:10 with a pH meter. For total soluble salt content determination, biochar was extracted with water, and the supernatant was dried and weighed. Elemental contents (i.e., C, H, O, N, and S) were determined with an elemental analyzer (VARIO EL Cube, Elementar, Germany). Total P (TP) was measured using the vanadium molybdate blue colorimetric method. Total potassium (TK) was measured by flame photometry.

2.4. Data Analysis and the Entropy Weight TOPSIS Method

In this study, the entropy weight TOPSIS method followed reference [35]. Data were processed using Microsoft Excel 2021 and analyzed using one-way analysis of variance (ANOVA). Figures were plotted using Origin 2021 and Adobe Photoshop 2022 software. The entropy weight TOPSIS method was implemented using MATLAB. The 16 cotton straw biochars, comprising the pristine biochar and the 15 acid-modified ones, were the alternatives, and the attributes of each alternative included pH, EC, total soluble salt content, C, H, O, N, S, H/C ratio, O/C ratio, TP, TK, SSA, APD, and TPV.

2.4.1. Attribute Weight Determination

As the attributes were different in dimension and order of magnitude, they were normalized before weights were calculated. For attribute x_{ij} with a positive value, it was normalized as follows:

$$x_{ij}^{'} = \frac{x_{ij} - x_j^{\min}}{x_j^{\max} - x_j^{\min}} \quad (1)$$

where x_{ij} is the value of the jth attribute of the ith biochar, $x_j^{\min}$ is the minimum of the jth attribute, $x_j^{\max}$ is the maximum of the jth attribute, and $x_{ij}^{'}$ is the normalized value of x_{ij}.

For attribute x_{ij} with a negative value, it was normalized as follows:

$$x_{ij}^{'} = \frac{x_j^{\max} - x_{ij}}{x_j^{\max} - x_j^{\min}} \tag{2}$$

As the normalized values of some attributes may be too small or negative, all normalized values were shifted as follows to avoid too small or negative values:

$$x_{ij}^{''} = H + x_{ij}^{'} \tag{3}$$

where H is the magnitude of the attribute shift, taken as 1 in this study.

Then, before entropy value calculation, the proportion (contribution degree) of the jth attribute in all attributes of the ith biochar was calculated as follows:

$$y_{ij} = \frac{x_{ij}^{''}}{\sum_{i=1}^{n} x_{ij}^{''}} \tag{4}$$

The entropy value of the jth attribute (e_j) was calculated as

$$e_j = -\frac{1}{\ln n} \sum_{i=1}^{n} y_{ij} \ln y_{ij} \tag{5}$$

The coefficient of variation for the jth attribute (g_j) was calculated as

$$g_j = 1 - e_j \tag{6}$$

Finally, the weight of the jth attribute (ω_j) was calculated as

$$\omega_j = \frac{g_j}{\sum_{j=1}^{m} g_j} \tag{7}$$

2.4.2. TOPSIS Model Development

"Ideal solution" and "negative ideal solution" are the two basic concepts of the TOPSIS model. The so-called ideal solution is a conceived optimal solution (scenario) with all attribute values reaching the best of the alternatives, whereas the negative ideal solution is a conceived worst solution (scenario) with all attribute values reaching the worst of the alternatives. All alternatives are compared with the ideal and negative ideal solutions. If one alternative is closest to the ideal solution and at the same time farthest from the negative ideal solution, it is the best of all alternatives.

Vectors were first normalized using Equation (1) or (2) and then transformed using the following equation to obtain the normalization matrix:

$$b_{ij} = \frac{x_{ij}^{'}}{\sqrt{\sum_{i=1}^{n} x_{ij}^{'2}}} \tag{8}$$

The normalization matrix was multiplied by weights to obtain a weighted normalization matrix (c_{ij}):

$$c_{ij} = \omega_j b_{ij} \tag{9}$$

The jth attribute value (c_j^*) of the ideal solution C^* was calculated as

$$c_j^* = \max_i c_{ij} \cdots j = 1, 2, \cdots, m \tag{10}$$

The jth attribute value (c_j^0) of the negative ideal solution C^0 was calculated as

$$c_j^0 = \min_i c_{ij} \cdots j = 1, 2, \cdots, m \tag{11}$$

The Euclidean distances of biochar i to the ideal (d_i^*) and negative ideal solutions (d_i^0) were calculated as

$$d_i^* = \left[\sum_{j=1}^{m} \left(c_{ij} - \max_i \{c_{ij}\} \right)^2 \right]^{1/2} \tag{12}$$

$$d_i^0 = \left[\sum_{j=1}^{m} \left(c_{ij} - \min_i \{c_{ij}\} \right)^2 \right]^{1/2} \tag{13}$$

Then, the comprehensive evaluation index C_i for biochar i was calculated as

$$C_i = \frac{d_i^0}{d_i^0 + d_i^*} \tag{14}$$

3. Results and Discussion

Acid modification is one of the most popular methods for improving biochar surface properties [38]. It can increase biochar SSA and the type and number of O-containing functional groups on the biochar surface. Acid modification also changes other physicochemical characteristics of biochar such as pH and elemental contents [24].

3.1. Biochar Morphological and Structural Changes

The SEM images showed that BC had a regular structure with many uniform micropores, whereas the acid-modified biochars had unregular structures with various-sized pores (Figure 2), indicating that the regular structure of cotton straw biochar was destroyed during acid modification, and consequently, micropores, mesopores, and macropores were formed.

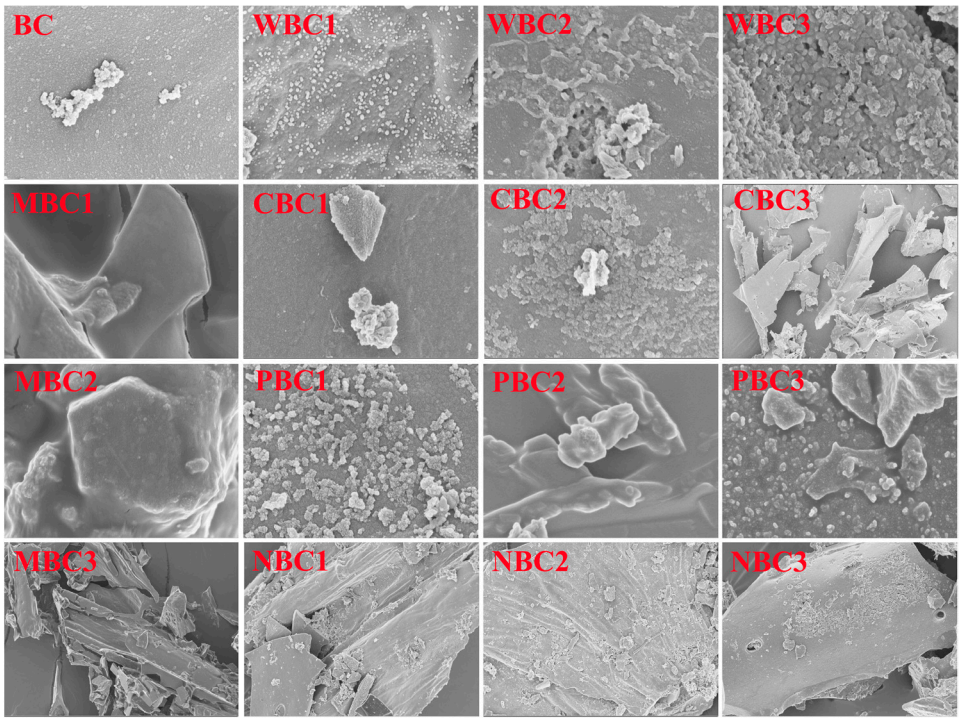


Figure 2. Scanning electron microscopy (SEM) images of the pristine and acid-modified cotton straw biochars.

Modification using wood vinegar and MSG wastewater significantly decreased the SSA of cotton straw biochar by 15.58–16.24 m^2 g^{-1} (82.7–86.2%) and 15.87–16.80 m^2 g^{-1} (84.2–89.2%), respectively, whereas modification using citric acid and nitric acid significantly increased the SSA of cotton straw biochar by 4.51–4.66 m^2 g^{-1} (23.9–24.7%) and 0.55–54.21 m^2 g^{-1} (2.9–287.7%), respectively (Table 3).

Table 3. The specific surface areas, average pore diameters, and total pore volumes of the pristine and acid-modified cotton straw biochars.

Property	BC	WBC1	WBC2	WBC3	MBC1	MBC2	MBC3	CBC1	CBC2	CBC3	PBC1	PBC2	PBC3	NBC1	NBC2	NBC3
Specific surface aera/($m^2 \cdot g^{-1}$)	18.84	2.60	3.26	2.82	2.04	2.97	2.40	18.03	23.35	23.50	39.73	7.28	1.92	62.89	73.05	19.39
Average pore diameter/(nm)	3.60	10.78	7.53	7.29	7.85	5.36	6.15	3.00	2.79	2.77	2.87	4.16	6.40	2.89	2.72	5.06
Total pore volume/($cm^3 \cdot g^{-1}$)	0.017	0.007	0.006	0.005	0.004	0.004	0.004	0.014	0.016	0.016	0.028	0.008	0.003	0.046	0.050	0.025

In contrast, modification using phosphoric acid significantly increased biochar SSA at the low dosage (PBC1) but significantly decreased biochar SSA at the high dosages (PBC2 and PBC3). These SSA changes demonstrate that different acidic modifiers lead to different changes in biochar SSA [40]. The reason for the higher SSAs of CBCs (i.e., CBC1–3) and NBCs as compared to BC might be that these strong acids rearranged the C-skeleton, removed the impurities from biochar surface, and provided acidic binding sites (e.g., phenolic hydroxyl, internal ether, and carbonyl groups), resulting in the increases in SSA and functional groups [41,42]. Biochar SSA increase caused by modification with a strong acid was also documented by Zhao et al. [43,44]. APD changes were in the opposite direction of SSA changes. Compared to BC, the APDs of WBCs and MBCs were greatly increased, whereas those of CBCs and NBCs were decreased. The APD of PBC was decreased at the low dosage of phosphoric acid (PBC1) but increased at the high dosages of phosphoric acid (PBC2 and PBC3). The opposite changes in SSA and APD demonstrate that more small pores lead to a higher SSA. TPV changes were generally consistent with SSA changes. TPV changes may be related to the etching effect of the acidic modifiers during modification [45–47]. Taken together, biochar SSA, APD, and TPV changes might be related to modifier concentration and acidity.

3.2. Biochar Surface Functional Group Changes

The FTIR spectra of all biochars showed a peak at 3400 cm^{-1} (Figure 3), which was ascribed to the vibration of alcoholic and phenolic –OH groups bonded by intermolecular hydrogen bonds [48,49]. The peaks at 1585 cm^{-1} and 1400 cm^{-1} were due to the stretching vibration of C=C and C=O, respectively [50,51]. The peaks at approximately 1158 cm^{-1} and 875 cm^{-1} were assigned to C-O and aromatic C-H, respectively [52]. Compared to BC, the peaks associated with O-H, C=O, and C-O groups in the spectra of acid-modified biochars, MBCs and WBCs in particular, were more intensive, indicating that there were more such O-containing functional groups on the surfaces of acid-modified biochars, which might be a result of hydroxylation and oxidation during acid modification [53]. The formation of these acid groups was the primary reason for the changes in the chemical properties of biochars. Liang et al. (2015) [54] found that modifying biochar with organic acid can reduce the BET specific surface area and total pore volume of biochar, and more oxygen-containing functional groups such as O-H, C=O, and C-O are formed on the surface, which is consistent with the results of WBC and MBC in this study. In addition, the C=O peak in the spectra of PBCs shifted to a higher wavenumber, and the C-H peak in the spectra of MBCs shifted to a lower wavenumber, indicating that π bonds or hydrogen bonds might have formed on the biochar surface [55].

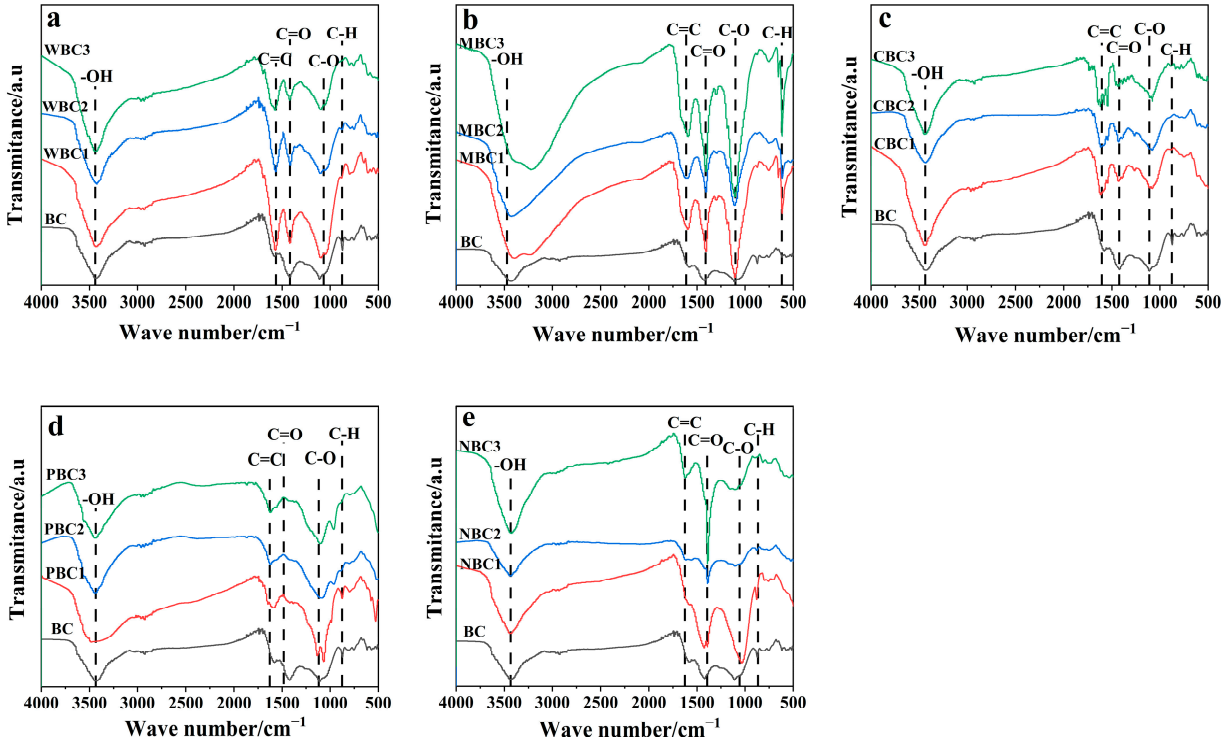


Figure 3. Fourier-transform infrared (FTIR) spectra of the pristine and acid-modified cotton straw biochars.

3.3. Biochar pH and Total Soluble Salt Content Changes

As shown in Figure 4a, acid modification led to decreases in the pH of cotton straw biochar, and the magnitudes of decrease followed the general order of PBCs > MBCs > WBCs > CBCs > NBCs. Phosphoric acid modification significantly decreased the pH of cotton straw biochar by 5.71–7.88 units. For the same modifier, a higher dosage (i.e., a smaller biochar:modifier ratio) led to a larger decrease in the pH of cotton straw biochar. Of the five modifiers, citric acid and phosphoric acid had the most striking dosage effect on the pH of cotton straw biochar. Sahin et al. (2017) used H_3PO_4 and HNO_3 and their combination to modify livestock biochar [56]. The experimental results showed that acid modification before biochar pyrolysis had no significant effect on the pH of biochar. However, acid modification after biochar pyrolysis can significantly reduce pH, which may be potentially beneficial for use in alkaline soils. This is consistent with the results of this study using PBC and NBC with different carbon–liquid ratios to reduce pH [56]. Some studies have shown that biochar modification has no significant effect on reducing the pH value of alkaline soil or even slightly increasing it. For example, the pH value of biochar modified by HCl decreased from 10.21 to 7.26, and the pH value of alkaline soil increased when 1% acidified biochar was applied to the soil with pH 7.73 [57]. This may be related to the exposure of more basic functional groups and minerals after modification [58]. In this study, the pH values of WBC3, MBC3, CBC3, PBC3, and NBC3 were 1.46, 0.56, 5.14, 3.83, and 0.76 units lower than those of WBC1, MBC1, CBC1, PBC1, and NBC1, respectively. These results demonstrate that not only modifier type but also modifier dosage influences the pH of modified biochar [59]. pH decrease may be due to the neutralization of alkaline groups, the generation of oxygenated functional groups [60–62], and the changes in polarity, surface charge, and backbone electron density of cotton straw biochar [63].

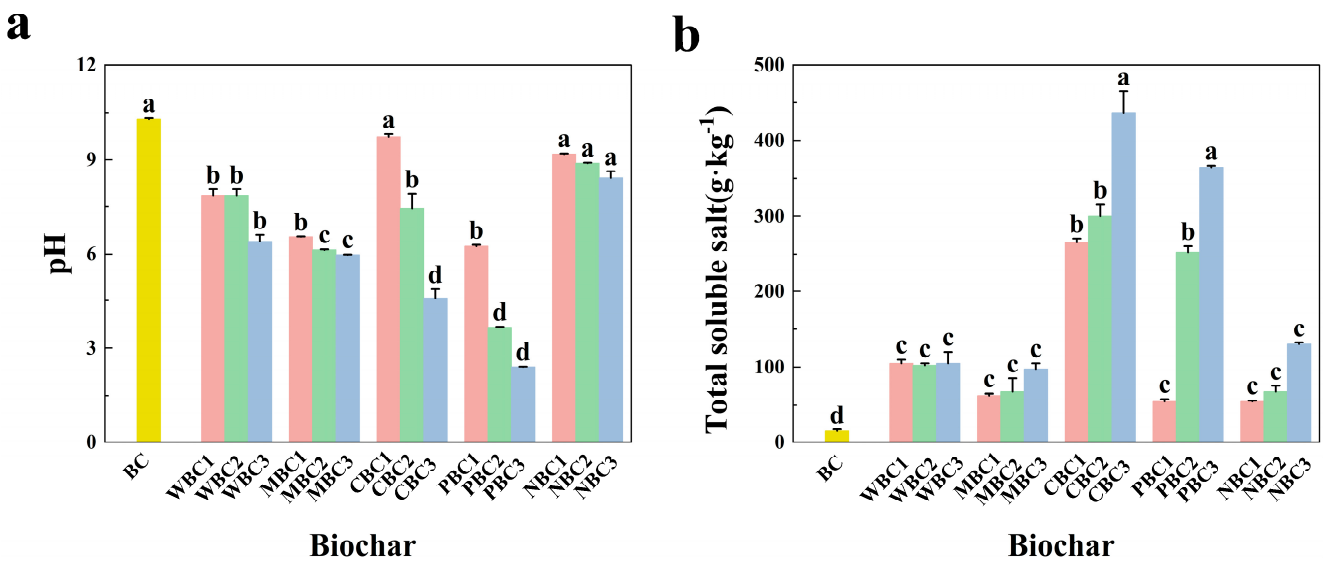


Figure 4. pH values and total soluble salt contents of the pristine (BC) and acid-modified cotton straw biochars. Note: Different letters above the bars indicate least significant difference (LSD) test at the 0.05 level between biochars.

The total soluble salt content of cotton straw biochar was significantly increased by acid modification (Figure 4b). The magnitudes of increase in total soluble salt content followed the general order of CBCs > PBCs > WBCs > NBCs > MBCs. The CBCs had very high total soluble salt content, 250–437.5 g kg^{-1} higher than that of BC. Similarly, not only modifier type but also modifier dosage influenced the total soluble salt content of modified cotton straw biochar, which increased with increasing modifier dosage. Sahin et al. (2017) found that H_3PO_4-modified biochar slightly increased the amount of EC, which is very similar to the results of this study [56]. They believe that this may be due to the reaction between H_3PO_4 and soluble minerals such as Ca, Mg, Fe, Zn, and Mn to form insoluble phosphate. The contents of water-soluble P, K, Ca, Mg, Fe, Zn, Cu, and Mn increased significantly [56]. Some researchers believe that this may be due to the increased functional groups on the biochar surface, which provide more binding sites for cations [64,65]. Although the PBCs displayed larger pH decreases than the CBCs, they displayed smaller increases in total soluble salt content, indicating that they had smaller ion-exchange capacities.

3.4. Biochar Elemental Content Changes

Compared to BC, the TP contents of WBCs, MBCs, CBCs, and NBCs were slightly lower or higher, whereas those of PBCs were 5.8–10.1 times higher. The strikingly higher TP contents of PBCs were clearly due to the P introduction by the modifier. Acid modification did not cause much change in the TK content of biochar, with 0.4–59.3% increase or decrease.

Compared to BC, the C contents of all acid-modified biochars, except NBC1 and NBC2, were decreased by 13–36% (Table 4), which might be due to biochar oxidation during modification with strong acids as oxidation is usually accompanied by C loss [66]. The H contents of MBCs were 77.2–113.0% higher than that of BC, whereas the differences between BC and the other four types of modified biochars were much smaller (0.5–15.8%). Modification with wood vinegar, citric acid, phosphoric acid, and nitric acid caused increase or decrease in the O content of cotton straw biochar, depending on modifier dosage, whereas modification with MSG wastewater led to consistent increases (64.8–88.3%) in the O content of cotton straw biochar, regardless of modifier dosage. The N content of WBCs, CBCs, and PBCs was 16.0–38.2% lower than that of BC, whereas that of MBCs and NBCs was 276.3–426.0% and 27.5–144.3% higher than that of BC, respectively. Modification with wood vinegar, citric acid, and phosphoric acid caused increase or decrease in the S content of cotton straw biochar, depending on modifier dosage, whereas modification with MSG

wastewater led to consistent increases (827.1–1204.2%) and modification with nitric acid led to consistent decreases (16.7–37.5%) in the S content of cotton straw biochar, regardless of modifier dosage. The reason for the markedly higher N and S contents of MBCs was that MSG wastewater has high concentrations of ammonium and sulfate. Similar changes in the C, H, O, N, and S contents of biochar after acid modification were also reported by Seredych et al. (2008) [67]. The H/C ratio can be used as an indicator of biochar aromaticity. A higher H/C ratio indicates a lower aromaticity of biochar [67–69]. Compared to the NBCs, the H/C ratios of MBCs were 133.3–150% higher, indicating that the MBCs were less aromatic than the NBCs. Fang et al. (2019) [70] pointed out that a low H/C ratio is associated with a low C loss rate and a low oxidation level of the modified biochar. The O/C ratio can reflect the relative concentration of the O-containing functional groups of biochar [71]. The O/C ratio of MBCs was 0.55–0.71, which was much higher than that of the other biochars, indicating that modification using MSG wastewater had introduced more O-containing functional groups to the cotton straw biochar than the other four modification methods. This was clearly supported by the FTIR spectra (Figure 3). The peaks of C=O and C–O showed much higher intensities in the spectra of MBCs than in those of the other biochars. In conclusion, MSG wastewater modification reduced the C content and increased the O content of cotton straw biochar by 22.2–31.8% and 64.8–88.3%, respectively. Consequently, the MBCs had higher concentrations of O-containing functional groups and lower degrees of aromatization compared to BC, indicating that there were more exchangeable active sites on the MBCs, which is favorable for water and nutrient retention and pollutant immobilization in soil [72].

Table 4. Elemental contents and atomic ratios of H/C and O/C of the pristine and acid-modified cotton straw biochars.

Content or Ratio	BC	WBC1	WBC2	WBC3	MBC1	MBC2	MBC3	CBC1	CBC2	CBC3	PBC1	PBC2	PBC3	NBC1	NBC2	NBC3
TP/(g·kg^{-1})	5.22	4.34	4.01	3.62	6.46	6.60	6.75	3.91	3.42	3.63	35.44	57.72	48.34	6.01	5.63	4.57
TK/(g·kg^{-1})	33.80	40.35	33.37	29.47	26.52	24.22	23.06	31.44	33.92	34.04	32.00	28.19	22.71	50.09	53.84	25.98
C/(%)	57.19	49.52	45.26	36.50	44.52	43.13	38.98	42.88	42.01	42.73	45.14	44.27	39.15	63.94	64.05	44.58
H/(%)	1.84	2.10	2.02	1.75	3.26	3.32	3.92	1.70	1.63	1.96	1.88	2.05	2.02	1.89	1.83	1.55
O/(%)	14.67	11.75	24.66	12.10	24.70	24.18	27.63	10.17	15.10	14.29	13.33	19.14	26.85	14.80	18.70	17.66
N/(%)	1.31	1.10	0.99	0.81	4.93	5.30	6.89	0.93	0.91	0.93	1.05	1.08	0.96	1.67	2.28	3.20
S/(%)	0.48	0.59	0.65	0.46	4.45	4.58	6.26	0.56	0.43	0.49	0.41	0.44	0.51	0.35	0.40	0.30
H/C	0.03	0.04	0.05	0.05	0.07	0.08	0.10	0.04	0.04	0.05	0.04	0.05	0.05	0.03	0.03	0.04
O/C	0.26	0.23	0.55	0.33	0.55	0.56	0.71	0.24	0.36	0.33	0.30	0.43	0.69	0.23	0.29	0.40

3.5. Biochar Agronomic Potential

In this study, 15 biochar attributes, namely, pH, EC, total soluble salt, TP, TK, C, H, O, N, S, H/C atomic ratio, O/C atomic ratio, SSA, APD, and TPV, were selected for biochar agronomic potential evaluation and the entropy weight method was used to determine the weights of these attributes. The entropy values and weights of the attributes are shown in Table 5.

Of all the attributes, TP, N, and S showed the highest weights, indicating that of the 15 attributes, TP, N, and S have the greatest influence on the evaluation of biochar agronomic application potential and decision making, and that the nutrient supplying capacity of biochar plays an important role in the agronomic potential of biochar in alkaline soils. Similarly, in the study of Zhang et al. (2018), yield, ash content, pH, nutrient contents, ion-exchange capacity, and other properties were selected as attributes to evaluate the agronomic potential of cow dung biochars prepared at different pyrolysis temperatures and times, and the entropy weight TOPSIS model was used to determine the weights of the attributes [32]. Xing et al. (2022) [73] reported the physicochemical properties of biochars prepared from different raw materials and at different pyrolysis temperatures, and SSA, pore volume, H/C ratio, N content, and pH were selected as attributes for gray correlation analysis. In addition, the potential of the biochars as slow-release carriers for biochar-based fertilizers was evaluated based on biochar physicochemical properties and production costs [73]. Both the gray correlation method used in their study and the TOPSIS method used in this study are comprehensive evaluation methods. As the nature of each

attribute is different, evaluation methods based on a single attribute are prone to causing errors. In contrast, comprehensive evaluation methods such as the entropy weight TOPSIS method used in this study can objectively reflect the weight of each attribute. Therefore, the credibility of the evaluation result is ensured.

Table 5. The entropy values, weights, and coefficients of variation in the attributes selected for biochar agronomic potential evaluation.

Attribute	Entropy Value	Weight	Coefficient of Variation
pH	0.99	0.04	0.01
EC	0.99	0.07	0.01
Total soluble salt	0.99	0.06	0.01
TP	0.99	0.09	0.01
TK	0.99	0.06	0.01
C	0.99	0.06	0.01
H	0.99	0.06	0.01
O	0.99	0.06	0.01
N	0.99	0.08	0.01
S	0.99	0.08	0.01
H/C ratio	0.99	0.05	0.01
O/C ratio	0.99	0.07	0.01
Specific surface aera	0.99	0.07	0.01
Average pore diameter	0.99	0.07	0.01
Total pore volume	0.99	0.07	0.01

The agronomic potential evaluation using the entropy weight TOPSIS model showed that of the 15 modified biochars, CBC1–3 and WBC3 had a lower agronomic application potential than the pristine biochar. The low agronomic application potential of CBCs might be due to their high total soluble salt contents, which are not favorable for plant growth. The MBCs had the highest potential for agronomic application, and the potential of the three MBCs was in the descending order of MBC3 > MBC2 > MBC1 (Figure 5). The higher agronomic application potential of MBCs was well supported by the characterization and physicochemical analysis results presented and discussed in the previous sections.

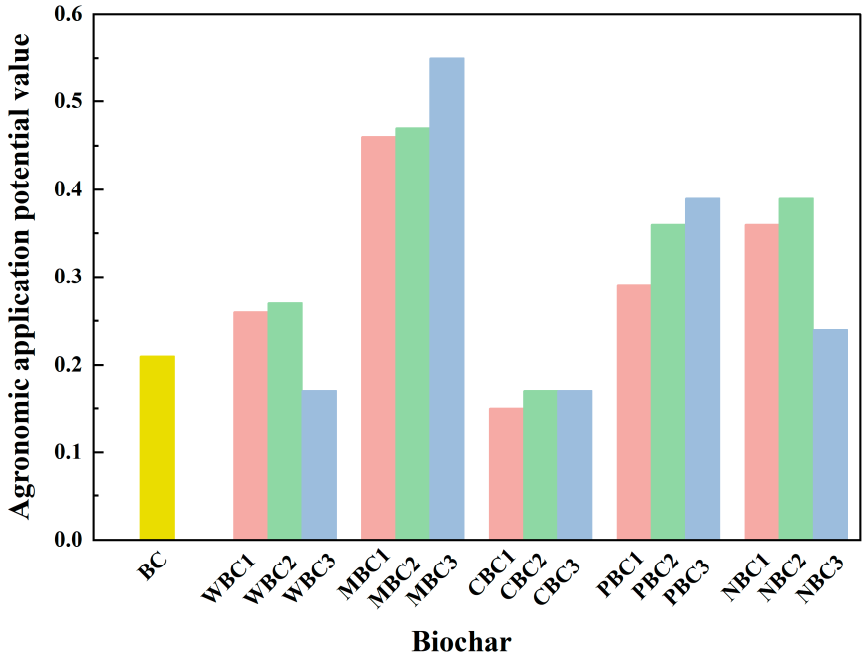


Figure 5. The agronomic application potential values of the pristine and acid-modified cotton straw biochars.

4. Conclusions

In this study, cotton straw biochar was modified with five different acidic materials, namely, wood vinegar, MSG wastewater, citric acid, phosphoric acid, and nitric acid, at different modifier dosages. The entropy weight TOPSIS model was used to evaluate the agronomic application potential of modified biochars in alkaline soils. The results showed that acid modification significantly reduced the pH of cotton straw biochar, with the pH values of PBCs being the lowest. According to the entropy weight TOPSIS model, the MBCs had the highest agronomic application potential, and the potential of the three MBCs was in the order of MBC3 > MBC2 > MBC1. Therefore, cotton straw biochar can be modified with MSG wastewater to improve its agronomic application potential in alkaline soils. This study provides a way of improving the agronomic application potential of biochar for use in alkaline soils and a way of beneficially utilizing agricultural wastes (e.g., cotton straw) and industrial wastes (e.g., MSG wastewater).

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Nomenclature

Biochar	Abbreviations
Wood-vinegar-modified biochar	WBC
Monosodium-glutamate (MSG)-wastewater-modified biochar	MBC
Citric-acid-modified biochar	CBC
Phosphoric-acid-modified biochar	PBC
Nitric-acid-modified biochar	NPC
Specific surface area	SSA
Average pore diameter	APD
Total pore volume	TPV

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