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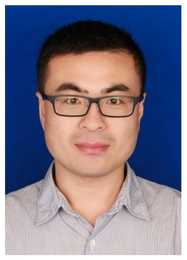
Effect of vermiculite modification and carbonization temperatures on carbon retention and stability of biochar derived from rice straw



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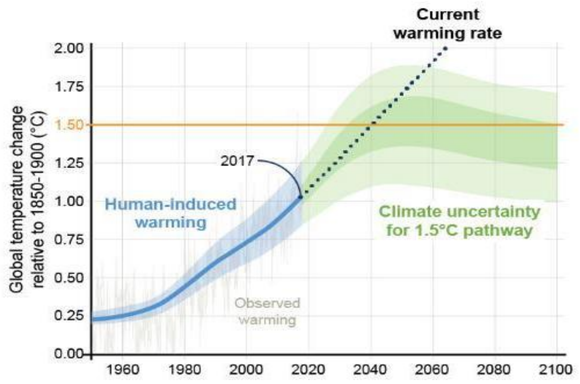
Introduction

Biochar is considered a promising material for locking CO_2 from the atmosphere, thus helping to alleviate climate change when returned to the soil. Biochar stability is the most decisive factor determining its C sequestration potential. Mineral modification may improve biochar characteristics, but systematic research on the effect of mineral modification on the C retention and stability of biochar and the associated mechanisms is limited.



(IPCC Special Report on Global Warming of 1.5°C, 2018)

Materials and methods

Vermiculite: $(Mg,Fe,Al)_3[(Si,Al)_4O_{10}(OH)_2]\cdot 4H_2O$, analytical reagents

The vermiculite was mixed with rice straw at a ratio of 1:4 (w/w).

Rice straw | Vermiculite | Modified biochar

Biochar yield: $Y = (M_s - M_m) / M_{bm} \times 100$

C retention ratio: $R = (Y \times C_{bc} / C_{bm}) \times 100\%$

Biochar heat stability is represented by the thermal weight loss ratio of C in biochar, which was measured according to the mass loss of C in the biochar samples by a thermogravimetric analyzer (Q50, TA, USA). The chemical stability of biochar was determined by chemical oxidation treatment, in which experimental $K_2Cr_2O_7$ was used to assess the labile fraction of C in the biochar samples.

Results

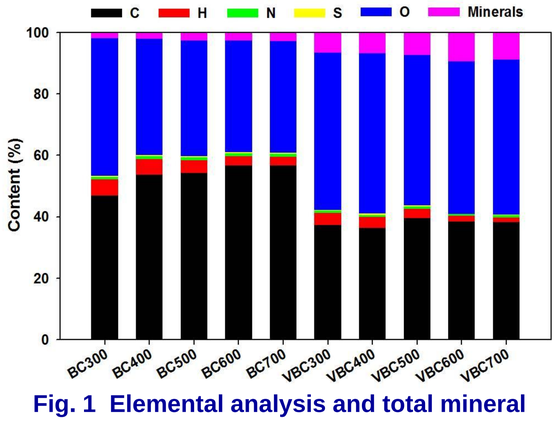


Fig. 1 Elemental analysis and total mineral contents of biochar

● The C and total mineral contents of all the biochars increased with increasing temperature, whereas the H and O contents decreased. After modification, the C content decreased, whereas the mineral content increased.

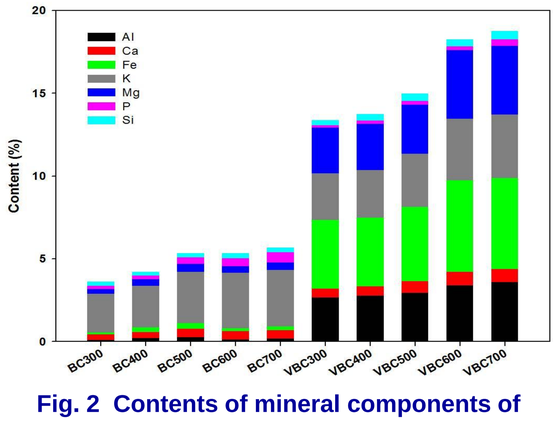


Fig. 2 Contents of mineral components of biochar

● The unmodified biochar is rich in mineral components, such as Al, Ca, Fe, K, Mg, P, and Si. After vermiculite modification, the Al, Fe, Mg, and Si contents increased with increasing temperature.

Table 1 Yield, C retention ratio, pH, and stability of biochar

Biochar	Yield (%)	C retention ratio (%)	pH	C thermal weight loss rate (%)	H/C atomic ratio	C oxidation loss rate (%)
BC300	55.5	75.6	5.56	75.4	1.36	51.8
BC400	53.9	71.7	7.04	68.6	1.16	48.1
BC500	42.7	62.5	7.96	58.7	0.92	30.4
BC600	35.3	54.0	10.2	34.8	0.66	10.2
BC700	34.5	51.9	10.5	32.8	0.60	2.43
VBC300	68.6	84.7	6.06	43.3	1.27	58.0
VBC400	61.2	75.3	6.88	37.3	1.14	44.9
VBC500	52.8	70.6	7.85	38.3	0.91	24.3
VBC600	49.0	66.0	9.74	29.6	0.56	5.52
VBC700	46.6	63.0	9.86	18.6	0.51	2.03

● Biochar yield and C retention ratio decreased with increasing temperatures but increased after modification. The C thermal weight loss, H/C atomic, and C oxidation loss ratios of biochar were reduced with increasing temperature, indicating improved thermal, aromatization, and chemical oxidation stability.

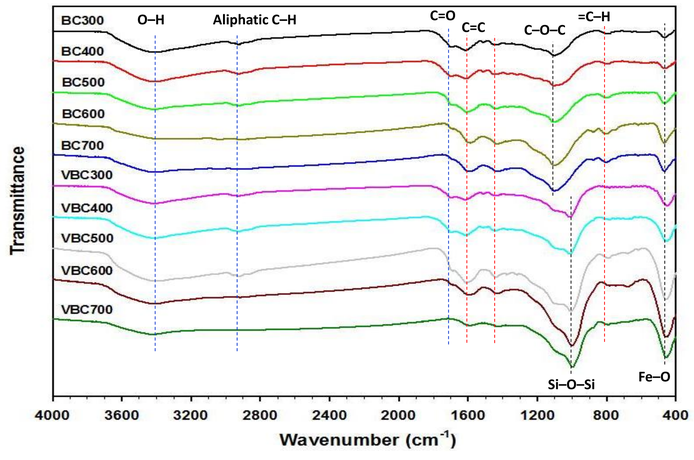


Fig. 3 FTIR spectra of biochar

● After modification, the vibration of Fe–O bonds on the biochar surface (450 cm^{-1}) was enhanced. The stretching vibration of C–O–C functional groups (1100 cm^{-1}) was weakened and replaced by Si–O–C or Si–O–Si groups (1000 cm^{-1}), indicating that more stable mineral organic complexes were formed on the surface of modified biochar.

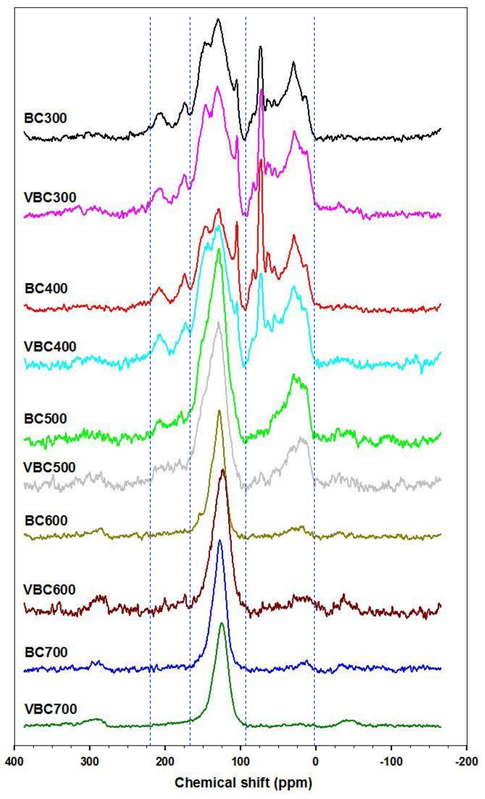


Fig. 4 ^{13}C CP-MAS NMR spectra of biochar

● The C-containing functional groups of rice-straw biochar mainly comprise aromatic C (165–95 ppm), which has a highly aromatic structure. Compared with high-temperature biochar (600 and 700 °C), low-temperature biochar (300–500 °C) also contains alkyl C (0–90 ppm) and carbonyl C (220–165 ppm) groups. Vermiculite modification accelerated the conversion rate of C from alkyl and carbonyl C to aromatic C.

Conclusions

● With increasing carbonization temperature, the C content of rice-straw biochar gradually increased, whereas the yield and C retention ratio gradually decreased.

● Compared with that of the unmodified biochar, the C content of the vermiculite-modified biochar decreased significantly, but the yield and C retention ratio increased significantly.

● The thermal weight loss, H/C atomic, and C oxidation loss ratios of biochar gradually decreased with increasing temperature, indicating that the thermal, aromatization, and chemical oxidation stability of biochar were enhanced.

●Vermiculite modification enhanced biochar stability by increasing the content of mineral components, promoting the formation of chemical bonds, such as Si–O and Fe–O, on the biochar surface, and improving the aromatization rate during carbonization.