

Spectral induced polarization of sand-biochar mixtures: Experiments, analysis and modeling

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Motivation and Methods

Biochar is the by-product of biomass pyrolysis and gasification in the absence of oxygen. Biochar attracts increasing research interest owing to its agricultural and environmental potential applications such as:

- improving soil functions
 - reducing emissions from biomass that would otherwise naturally degrade to greenhouse gases
 - promising long-term carbon sequestration
- Further research requires effective methods which allow investigating biochar in the laboratory and at field scale.

Spectral induced polarization (SIP) seems to have a potential to contribute with real-time and non-invasive measurements to a comprehensive assessment of biochar. SIP determines the effective complex electrical conductivity $\sigma^* = \sigma' + i \cdot \sigma''$.

Debye decomposition (DD) allows deconvolution of one SIP spectrum by superposition of a certain number (N) of elementary Debye spectra, where each of the N Debye spectra is characterized by a chargeability m_k , relaxation time τ_k and the DC resistivity ρ_0 . The normalized total chargeability is given by $M_n = \sum m_k / \rho_0$.

$$\rho^* = \rho_0 \left[1 - \sum_{k=1}^N m_k \left(1 - \frac{1}{1 + i\omega\tau_k} \right) \right]$$

An electrochemical SIP model developed by Wong (1979), suggests that "active ions" which can reduce or oxidize at the metal-electrolyte interface causes an leakage current when an external electrical field is applied. Therefore, the complex electrical conductivity of the particle σ_p is determined by the sum of surface conductivity σ_s and the effective conductivity produced by the redox reaction σ_r .

$$\sigma_p = \sigma_r + \sigma_s$$

On biochar, active species may be **active ions**, **neutral molecules** or **functional groups** at the surface. Most redox reactions on biochar are multistep processes.

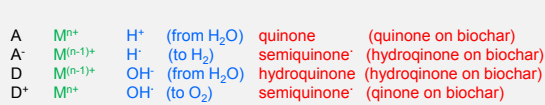
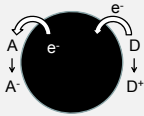


Figure 1 Reactions at the interface of electronically conductive particles of biochar

SIP spectra

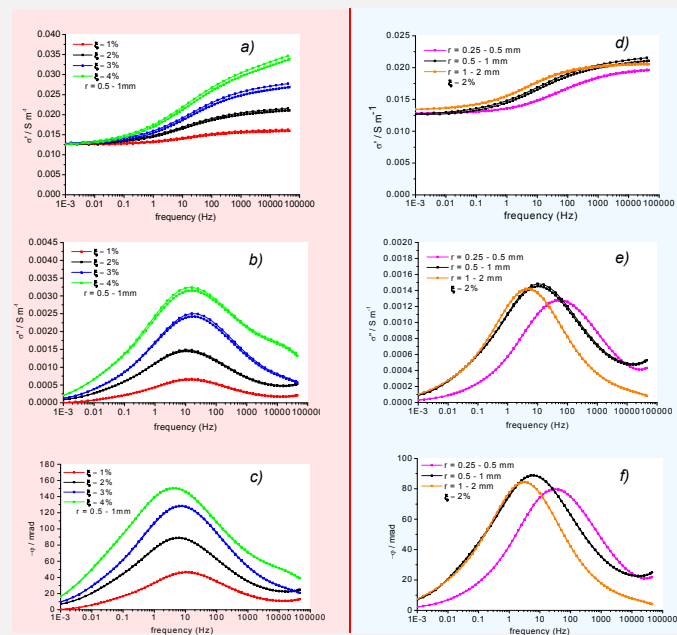


Figure 2 Frequency-dependent complex electrical conductivity (σ^*) of sand-biochar mixtures: (a), (b) and (c) are the real part, imaginary part and phase of σ^* of samples with various mass fraction but constant particle size of biochar, while (d), (e) and (f) are that of samples with various particle size but constant mass fraction of biochar. The particle size of the biochar has a clear influence on the shape and the peak frequency of the SIP response, whereas the fraction of biochar determines the magnitude and the maximum value of the spectra.

Materials and Measurement

Two sets of samples (mixtures of pure sand and biochar) were investigated. The biochar was obtained from pine woodchips by slow pyrolysis at 400 °C. Biochar of various particle sizes (r) and mass fractions (ξ) were added in the mixtures. The sample was flushed with 4 mM NaCl solution.

We used a sample holder with a height of 18 cm, an inner diameter of 3 cm and a four-point electrode array with 6 cm spacing between the electrodes. The electrical impedance of samples was measured from 1 mHz to 45 kHz.

Table 1: Mass fraction and particle size of biochar in samples

Set A Sample No.	Fraction of biochar (ξ)	Particle Size of biochar (r)	Set B Sample No.	Fraction of biochar (ξ)	Particle Size of biochar (r)
1	1%	0.5 – 1 mm	1	2%	0.25 – 0.5 mm
2	2%	0.5 – 1 mm	2	2%	0.5 – 1 mm
3	3%	0.5 – 1 mm	3	2%	1 – 2 mm
4	4%	0.5 – 1 mm			

Results

Debye decomposition

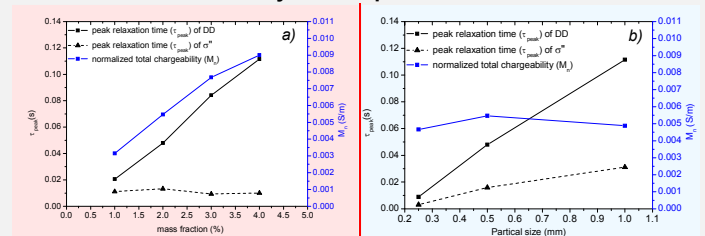


Figure 3 Peak relaxation time and normalized total chargeability of sand-biochar mixture: (a) shows the results of samples with various mass fraction but constant particle size of biochar, while (b) shows the results of samples with various particle size but constant mass fraction of biochar. It is interesting to note that τ_{peak} (DD) depends both on the particle size and the fraction of biochar.

Electrochemical SIP model

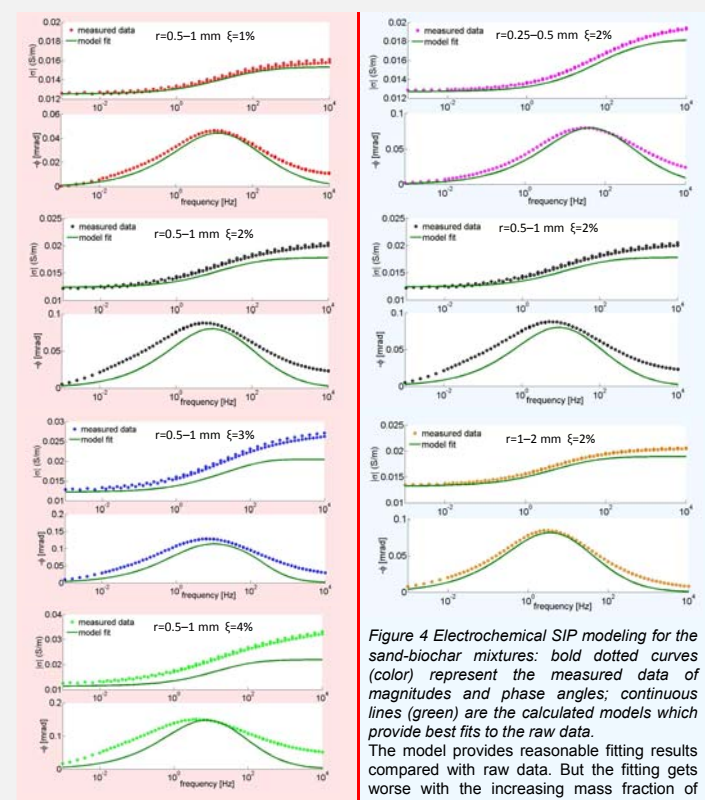


Figure 4 Electrochemical SIP modeling for the sand-biochar mixtures: bold dotted curves (color) represent the measured data of magnitudes and phase angles; continuous lines (green) are the calculated models which provide best fits to the raw data. The model provides reasonable fitting results compared with raw data. But the fitting gets worse with the increasing mass fraction of biochar.

References

- [1] Wong, J.
 An electrochemical model of the induced-polarization phenomenon in disseminated sulfide ores.
 Geophysics 1979, 44, 1245–1265.

Conclusions and Outlook

The results show that biochar in sand has significant polarization and an obviously characteristic SIP response. The particle size and the fraction of biochar has influence on the characteristics of the SIP signal. SIP might be an effective method to detect and characterize biochars in soil. The relationship between the properties of biochar and SIP response, and the modeling methods need to be further explored.