COMPARATIVE EPR ANALYSIS OF OXYGEN INTERACTIONS WITH PLANTS CARBONIZED AT DIFFERENT TEMPERATURES

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Abstract

Carbon materials, bamboo (Bambusa vulagris) and yucca (Yucca flaccida) pyrolysed at 550°C, 750°C and 950°C, were tested as oximetric probes by electron paramagnetic resonance spectroscopy at X-band (9.3 GHz). The following parameters of the spectra: amplitude, linewidth and g-factor, were determined. Influence of oxygen molecules O_2 on EPR spectra of the individual carbon materials was compared. Strong EPR spectra were recorded for samples carbonized at 550°C and weak signals were obtained for plants carbonized at higher temperatures: 750°C and 950°C. It was stated that amplitudes of EPR lines of all the carbonized plants decrease in the air environment compared to amplitudes of spectra measured in vacuum. This effect increases with degree of vacuum. Changes in the EPR spectra of samples studied in the air environment may be applied in medicine to determination of oxygen content in different cells. Because of strong resonance signals as oximetric probes we proposed bamboo and yucca carbonized at 550°C, and we rejected plants carbonized at 750°C and 950°C with low EPR signals.

Keywords: *carbonized plants, paramagnetic centers, paramagnetic oxygen molecules, electron paramagnetic resonance, EPR spectra, oximetry*

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Introduction

Paramagnetism of carbon materials depends on temperature of sample heating [1-11]. High concentration of paramagnetic centers and chemical structure indicate susceptibility of materials to oxygen. Carbon materials may be used as oximetric probes for biological systems [12-18]. Oximetry is a very important technique for determination of singlet oxygen formation during photodynamic therapy [19-20]. Photodynamic therapy of tumor cells is accompanied by intensive excitation of oxygen molecules to singlet state by laser irradiation. Singlet oxygen formation in cells is accompanied by decrease of amplitude of EPR lines of carbon probe [16-18]. New carbon oximetric probes are still searching and their chemical structure is studied.

The aim of this work was to find carbon materials for EPR spectroscopic oximetry in medicine. Carbon materials obtained from different types of pyrolysed plants were tested by the use of electron paramagnetic resonance (EPR) spectroscopy. The best oximetric probes characterize strong dependence of EPR spectra on oxygen contents in the environment. We compared interactions of paramagnetic centers of the individual samples with paramagnetic oxygen molecules O_2.

Materials and methods

Bamboo (Bambusa vulagris) and yucca (Yucca flaccida) pyrolysed at 550°C, 750°C, and 950°C were studied. Carbonization process was done in the neutral atmosphere.

The first derivative EPR spectra were measured with magnetic modulation of 100 kHz. The measurements were done by the use of RADIOPAN (Poznań, Poland) EPR spectrometer with microwave frequency of 9.3 GHz. Microwave frequency was detected by MCM102 recorder produced by EPRAD Firm (Poznań, Poland). Amplitudes (A), linewidths (ΔB_{pp}) and g-factors of the EPR lines were obtained. EPR spectra were measured with different attenuations [dB]: 15, 10, 5, and 0.5. EPR measurements were done for samples in air and in vacuum (900-10^{-5} mbar).

Results and discussions

No EPR lines were measured for the original plant samples. Probably low amount of paramagnetic centers exist in bamboo and yucca, but their concentration is negligible. During heating of plant materials chemical bonds are ruptured and paramagnetic centers appear in the samples. EPR spectra were obtained for all the studied carbonized materials. g-Values were in the range 2.0028-2.0030. Paramagnetic centers concentrations in the carbonized plants were about 10^{16}-10^{21} spin/g.

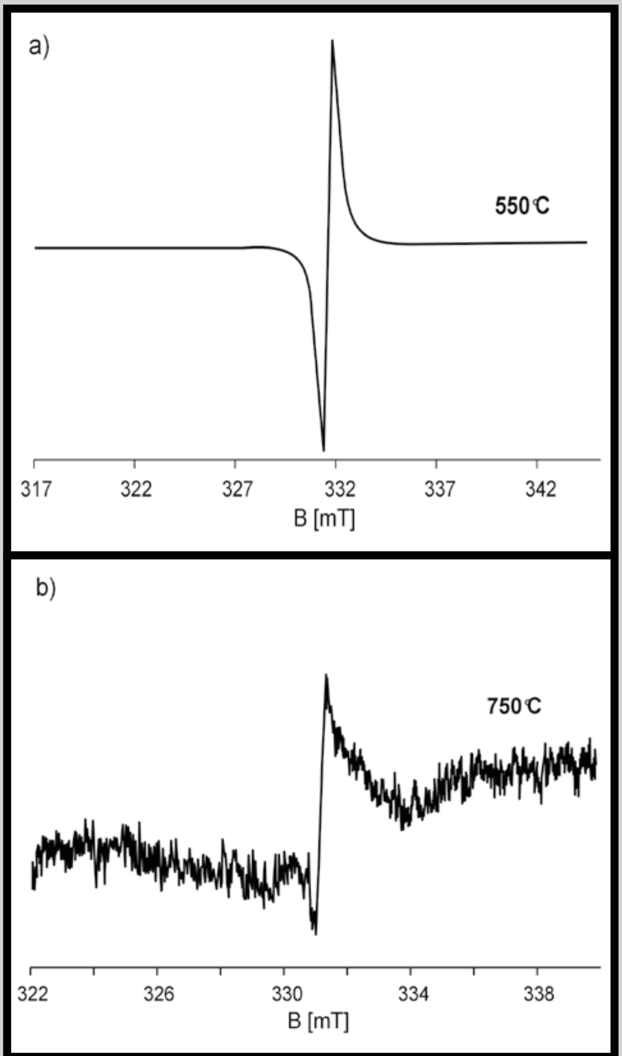

FIG.1. EPR spectra of bamboo carbonized at 550°C (a) and 750°C (b). Data for samples in air.

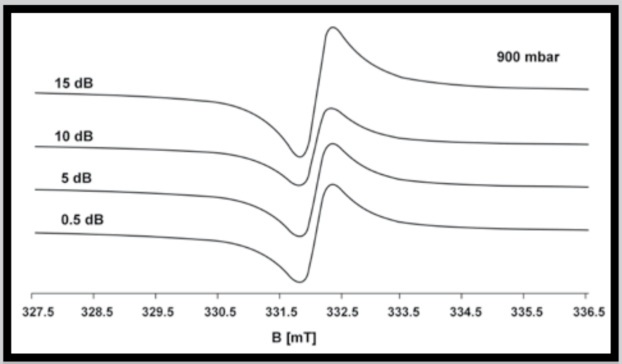

FIG.2. EPR spectra of yucca carbonized at 550°C for pressure of 900 mbar. Spectra were measured with attenuations of microwave power [dB]: 15, 10, 5, and 0.5.

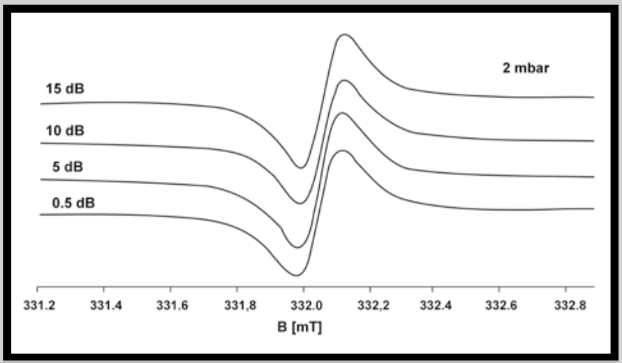

FIG.3. EPR spectra of yucca carbonized at 550°C for pressure of 2 mbar. Spectra were measured with attenuations of microwave power [dB]: 15, 10, 5, and 0.5.

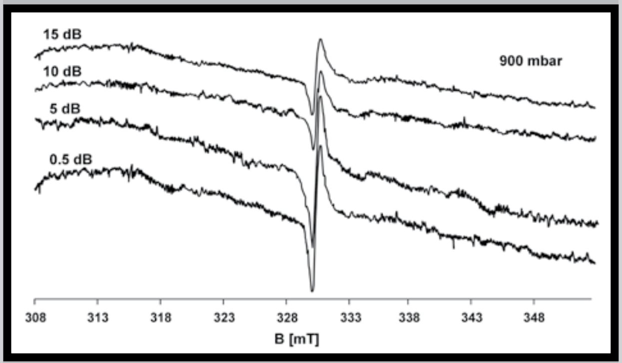

FIG.4. EPR spectra of yucca carbonized at 950°C for pressure of 900 mbar. Spectra were measured with attenuations of microwave power [dB]: 15, 10, 5, and 0.5.

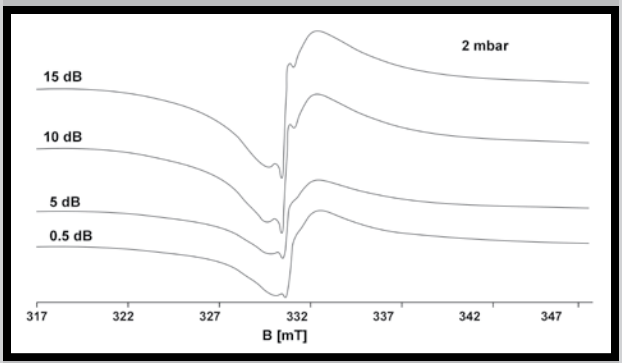

FIG.5. EPR spectra of yucca carbonized at 950°C for pressure of 2 mbar. Spectra were measured with attenuations of microwave power [dB]: 15, 10, 5, and 0.5.

Amplitudes of the spectra depend on temperature of plant heating. We measured strong EPR lines for bamboo and yucca pyrolysed at 550°C. The low amplitudes characterize resonance curves of plants carbonized at 750°C and 950°C. For example EPR spectra of bamboo heated at 550°C and 750°C for sample in air are compared in FIG.1. As one can see noisy spectrum is observed for samples heated at 750°C.

Exemplary EPR spectra of yucca pyrolysed at 550°C and 950°C for samples in vacuum are shown in FIGURES 2-3 and 4-5, respectively. Plants carbonized at 750°C and 950°C were rejected as oximetric probes. Their EPR signals were too low or revealed complex character. Complex structure of EPR spectra is clearly visible for yucca carbonized at 950°C.

We see two components differ in linewidths in these spectra (FIG.4-5). EPR spectra of this carbonized yucca is superposition of broad and narrow lines resulted from two types of paramagnetic centers in the sample. Similarity of these EPR spectra (FIG.4-5) with multi-component spectra of natural coal samples [11] is expected. Paramagnetic centers located in simple units consisting of a few aromatic rings are responsible for broad EPR component and π electrons delocalized on large aromatic structures give narrow component [11]. The data indicate that chemical structure of yucca carbonized at 950°C is more complicated in comparison to yucca heated at 550°C. Paramagnetic carbonized plants with multi-component EPR spectra should be rejected as oximetric probes, because calculations for such spectra are too complex.

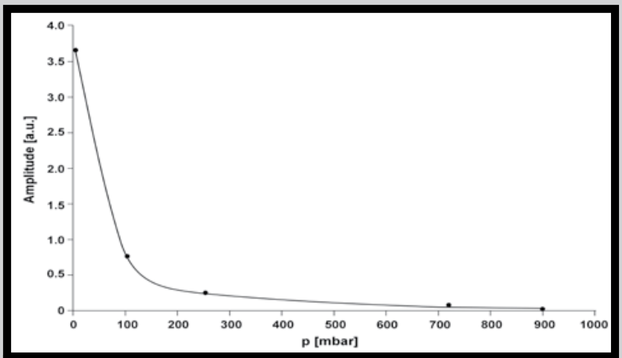

FIG.6. Influence of degree of vacuum (pressure p [mbar]) on amplitudes of EPR lines of yucca carbonized at 550°C. Attenuation of microwave power was 15 dB.

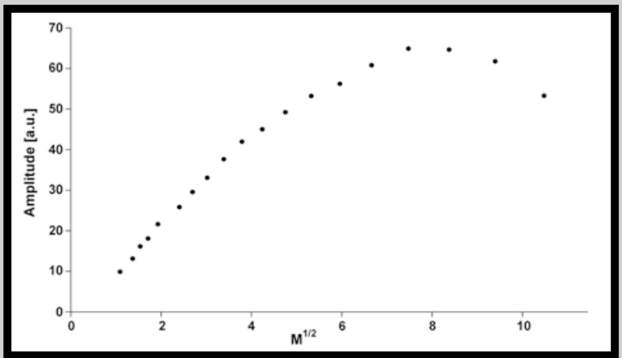

FIG.7. Influence of microwave power on amplitudes of EPR lines of yucca carbonized at 550°C for samples in vacuum (10^{-5} mbar).

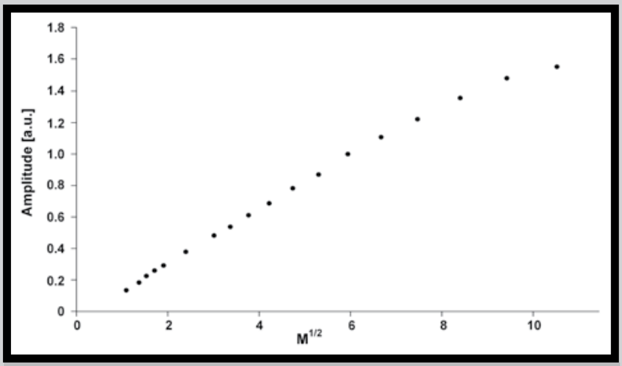

FIG.8. Influence of microwave power on amplitudes of EPR lines of yucca carbonized at 950°C for samples in vacuum (10^{-5} mbar).

As oximetric probes were proposed plants heated at 550°C with simple EPR spectra (FIG.2-3). Their EPR amplitudes strongly decrease with increasing of oxygen contents in the environment (FIG.6). Quasi-chemical bonds between carbon material and oxygen molecules are responsible for this effect. Exemplary correlation presented in FIG. 6 may be the reference curve for determination of oxygen content in the biological sample environment. In practice comparison of amplitudes of EPR spectra of carbon materials located in cell cultures and amplitudes in reference curves is necessary to obtain information about oxygen content in the tested cells.

Continuous microwave saturation of EPR technique was used to develop characteristic of aromatic structure of the studied carbonized materials. EPR spectra of samples carbonized at 550°C saturate at lower microwave powers than EPR spectra of plants heated at 750 and 950°C (FIG.7-8). It can be concluded that plants heated at 550°C proposed to oximetry contain lower condensed aromatic units as compared to samples heated at higher temperatures. Condensation of aromatic units led to decrease of paramagnetic carbon contents in these samples.

Conclusions

On the basis of electron paramagnetic resonance studies of carbonized bamboo and yucca in air and in vacuum the following conclusions may be drawn:

1. The studied plant materials carbonized at 550°C, 750°C, and 950°C are paramagnetic.
2. Strong EPR lines characterize the analysed samples carbonized at 550°C and weak EPR lines reveal samples carbonized at both 750°C and 950°C.
3. Paramagnetic centers of the plant materials heated at 550°C, 750°C and 950°C interact with paramagnetic O_2 molecules, what led to quenching of their EPR signals.
4. Decrease of amplitudes of the recorded EPR spectra is stronger for highest oxygen concentrations in the sample environment.
5. Because of strong EPR lines and dependence of their amplitudes on oxygen concentration, bamboo and yucca carbonized at 550°C is proposed as oximetric probe in medicine.

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