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Identification of the EPR signals of fig leaves (Ficus carica L.)

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The article is devoted to the study of the leaves of the fig (Ficus carica L.) tree is one of the most valuable trees of the Absheron Peninsula (Azerbaijan). Research on fig leaves growing in Mardakan and Nardaran areas of Absheron has been carried out on EPR spectrometer. Studies have shown that stressors cause the formation of nanophase particles of biogenic origin in living systems. These nanoparticles lead to the formation of magnetic properties in biological systems and the formation of the broad EPR signal that we first discovered in plants. It was found that the magnetic properties depend on the type of plant and the environmental conditions in which they live and the characteristics of EPR signals characterizing magnetic nanoparticles (amplitude, signal width, g factor, etc.) are strongly dependent on temperature and that this signal has magnetic anisotropy. Studies of fig leaves have shown that as a result of biomineralization under stress, they form magnetic nanoparticles of iron oxide. In addition, the high intensity of the broad EPR signal characteristic of nanophase magnetic particles detected in fig leaves growing in Mardakan area (Azerbaijan) indicates that the plant system in this area is more exposed to pollutants and the area is more environmentally polluted than Nardaran Area (Azerbaijan). The characteristic verve phase transition occurs at a temperature of 120-125 K in the behavior of parameters such as the amplitude of the magnetic resonance signal and the width of the magnetic resonance line. The results were confirmed by the messabauer method.

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KEYWORDS

Magnetic resonance; ficus carica; magnetic nanoparticles; EPR spectrometer.

Introduction

Magnetite (Fe_3O_4) and magemite (γ-Fe_2O_3) have a vital role in the functioning of living organisms and all of the sciences [1,2,3] and causing broad EPR signal and magnetization in natural organisms [4,5,6]. In our previous works, we studied the EPR spectra of leaves and seeds of various trees and shrubs growing in ecologically polluted areas of the

Absheron Peninsula, and the EPR spectra of seedlings of different types of plant seeds exposed to ionizing gamma radiation, and finally, we found the formation of Fe_3O_4 and γ-Fe_2O_3 nanoparticles in plants during stress, and the formation of anomalous magnetic properties in them. We have shown that these nanoparticles lead to the development of magnetic properties in biological organisms and the formation of a broad EPR signal, which was first detected in plants [7,8,9,10]. Therefore, we studied the biogenesis of Fe_3O_4 and γ-Fe_2O_3 nanoparticles in the leaves of figs from Absheron Peninsula (Azerbaijan). The Absheron Peninsula is rich in very valuable tree species. One of the most common of these is the fig (Ficus carica L.). Ficus carica L. is widespread in Azerbaijan, especially in Absheron, has decorative leaves and slightly elongated fruits. Scientists and botanists believe that among the most widespread subtropical fruit plants in the world, figs are the most fragrant, rich, nutritious and sweet fruit plant. The medicinal effects of fig leaves have been studied to some extent, and in folk medicine, dried leaves are used in the treatment of cardiovascular diseases by infusion or cooking [11, 12, 13, 14]. Physically and ecologically, fig leaves have not been studied much. With this in mind, fig leaves were chosen as the object when we were studying tree plants.

Experimental

General

Fig tree leaves, which are typical for the Absheron region, were examined at room temperature on a 3 cm range EPR spectrometer (Bruker-EMX, Germany). For this purpose, fig leaves, which are the objects of research, were collected from the territory of Nardaran and Mardakan settlements of Absheron in summer and autumn, dried at room temperature and their EPR spectra were recorded (Figure 1).

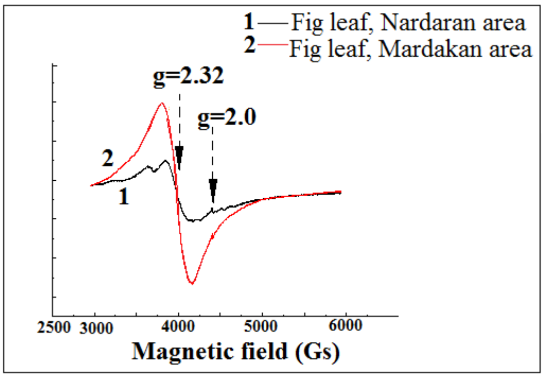

FIGURE 1 EPR spectra of fig leaves

EPR spectra were documented using EPR spectrometer (Bruker, Germany) X-band at normal temperature (297 K). The accuracy of the obtained results was confirmed by the Messbauer spectroscopy method.

Results and discussion

When EPR spectra were recorded, the samples were normalized per unit mass. It was found that three types of signals are recorded in the spectra of leaves (Figure 1). The main place in the detected spectra captures a wide EPR signal (g = 2.32). At the same time, a weak signal belonging to the trivalent iron complexes recorded in the samples (g = 3.4) and a signal of free radicals corresponding to g = 2.0023 are also observed. The extensive EPR signals we receive give us reason to say for the first time that iron oxide magnetic nanoparticles are formed on fig leaves growing in the Absheron Peninsula and they are generated as a result of biomineralization under the effect of stress factors (eg, humidity, heavy metals, pesticides, herbicides, various industrial wastes, temperature, etc.). At the same period, the high intensity of the broad EPR signal of iron oxide magnetic nanoparticles recorded in samples and collected from the Mardakan area suggests that the living system in this area is more exposed to pollutants and that the area is more environmentally polluted than Nardaran [15, 16, 17, 18]. In addition, to study the characteristics of a specific broad-spectrum EPR signal characterizing an iron oxide nanoparticle, we studied the EPR signals of plants by changing the parameters of the radiospectrometer and determined that this signal had magnetic anisotropy (Figure 2).

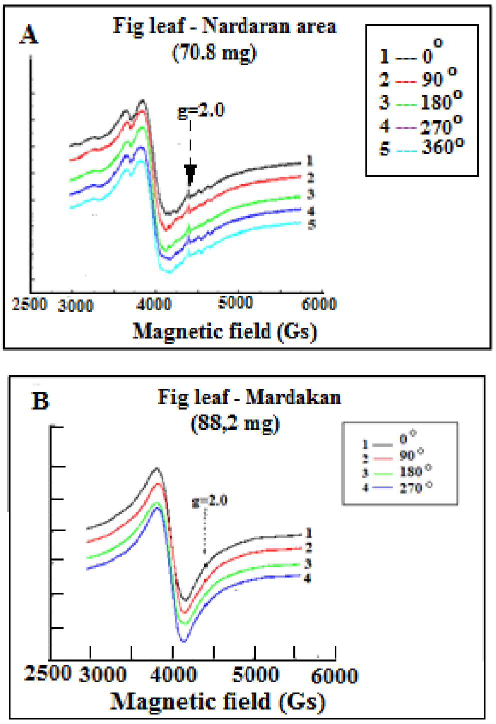

FIGURE 2 EPR spectra at different angular variations of fig leaves collected from Nardaran and Mardakan areas (A and B)

Thus, when researching the samples by rotating the glass ampoule, in which they were located, at different angles (90°, 180°, 270°, 360°), we observed that the shape of the EPR signal changed to some extent (Figure 2). We determined that the EPR signal shifts slightly to the left when the samples are rotated 90°, 180°, 270°, 360° in the resonator of the spectrometer. Such behavior of signals has been found for magnetite (Fe_3O_4), magemit (γ-Fe_2O_3) and superparamagnetic nanoparticles. This indicates that the paramagnetic centers responsible for the EPR signal have a complex structure [19,20,21]. In Figure 3 shows the EPR spectra of fig leaves depending on different microwave powers (0.5 - 200 mW) at room temperature. It was found that the intensity of the EPR signals taken from the samples, especially the signal of free radicals (g = 2.0023), strongly depends on the power of the ultra-high frequency (UHF).

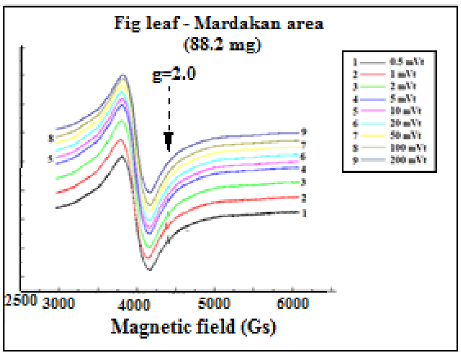

FIGURE 3 Spectras of dependence of fig leaves on UHF power (0.5 - 200 mVt)

Candida experiments with fig leaves have led to important and new results. For this reason, for a broad identification of the received signals, and for giving them more complete characteristics, we investigated the temperature dependence of these signals. It was found that these spectra change depended on the temperature (Figure 4).

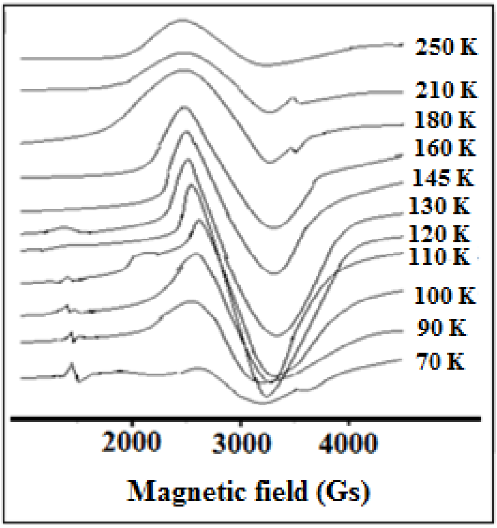

FIGURE 4 Temperature dependence of EPR spectra of fig leaves in the range 70K - 250K

When the temperature decreases from normal temperature to 120-125 K, signal amplitude increases rapidly and reaches its maximum at T ≈ 120-125 K. During subsequent decreases in temperature, the amplitude of the signal decreases sharply (Figure 4). Due to the change in the values of intensities, we can say that the magnetization for Fe_3O_4 increases linearly to 120-125 K. However, with a subsequent decrease in temperature, the magnetization gradually begins to decrease. As can be seen from Figure 4, the magnetization curve reaches its maximum value at 120-125 K, and then decreases sharply. Based on the temperature dependence of typical EPR signals, the temperature dependence of the integrated intensity (Figure 5) and the width of the signal (Figure 6) were obtained, and a non-monotonic dependence was observed. Changes in the behavior of the parameters in the 120-125 K indicate a significant change in the structure of the magnetic centers (Figures 5 and 6).

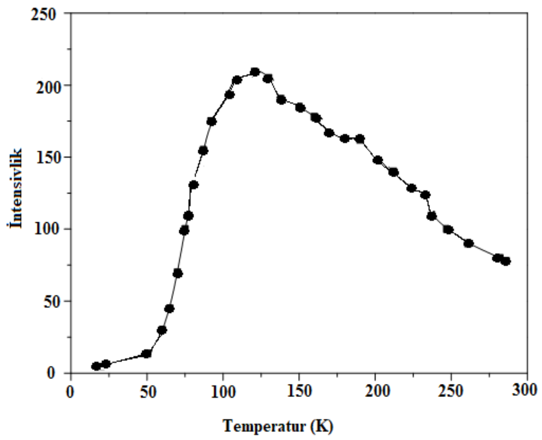

FIGURE 5 Temperature dependence of EPR signal intensity

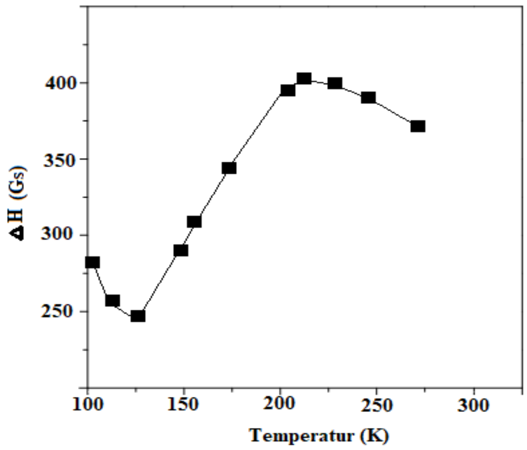

FIGURE 6 Temperature dependence of EPR signal width

In addition, the shape of the signal line varies from asymmetric to Lorence when it is above this temperature. The behavior of these characteristics allows us to say that the Vervey phase transition is observed in magnetite. During this phase, the crystalline structure of the magnetite is transformed from a cubic to a monoclinic form [22, 23]. The behavior of these characteristics allows us to say that the Vervey phase transition is observed in magnetite. During this phase, the crystalline structure of the magnetite is transformed from a cubic to a monoclinic form [23,24]. When studying the temperature dependence of the signal intensity and width, we observed the behavior of superparamagnetic nanoparticles in the investigated temperature range, since the signal width approaches a minimum at 120-125 K. A similar decrease in the g-factor at low temperatures was previously observed in magnetite nanoparticles placed in a polymer matrix and was explained by the adaptation of the system to spin glass [25]. Only sufficiently large particles (greater than 10 μm) have been characterized by such low-temperature anomalies [26,27]. The changing behavior of the parameters indicates that the system may have two types of particles that differ in size [28]. The critical temperature for both types of particles is ≈ 125-130 K. At this temperature we observed a change in the behavior of the g-factor, a change in the signal intensity, and also the minimum signal width. It is known that the expansion of the EPR signal and its displacement into a smaller magnetic field during a decrease in temperature is the characteristic of superparamagnetic nanoparticles [29]. The accuracy of the obtained results was confirmed by the Messbauer spectroscopy method (Figure 7). The 1st doublet in Figure 7 corresponds to Fe^{3+} atoms. Their relative number is 76%. The 2nd doublet corresponds to Fe^{2+} atoms. Their relative amount is 24%. The Lawrence form of the line was used for both doublets. The phase of magnetic regularity was not observed. Particles made of iron atoms are in a paramagnetic or superparamagnetic state. Thus, research on one of the valuable plants of Absheron peninsula (Azerbaijan), *i.e.* fig leaves, showed that as a result of biomineralization.

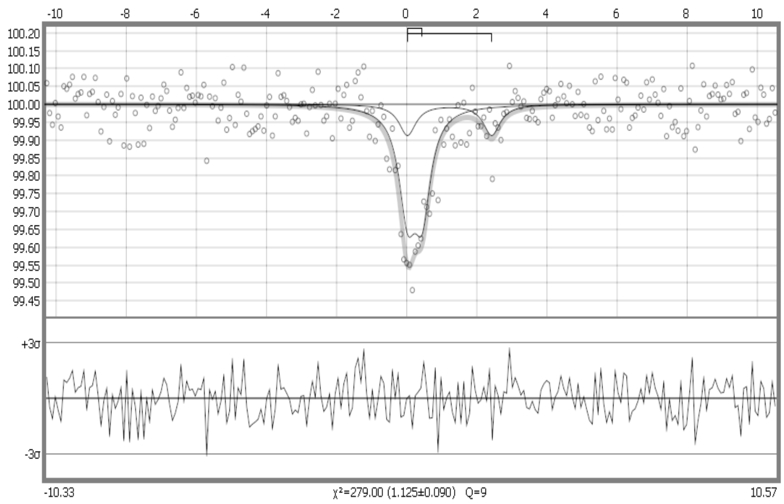

FIGURE 7 Messbauer spectra of fig leaves

Under stress conditions, they formed Fe_3O_4 and γ-Fe_2O_3 nanoparticles. In addition, the high intensity of the broad EPR signal characteristic of nanophase magnetic particles found on fig leaves in Mardakan indicates that the plant system in this area is more exposed to pollutants and that this area is more environmentally polluted than Nardaran. Experiments have shown once again that stress factors cause the formation of nanophase particles of biogenic origin in living systems. These nanoparticles lead to the broad EPR signal and magnetization in biological organisms that we first discovered in plants [7,15,31,32]. It was found that the type of plant and the environmental condition in which they live have an important role in the magnetic properties. It was found that the characteristics of EPR signals (amplitude, signal width, g- factor, etc.) that characterize magnetic nanoparticles are strongly dependent on temperature and that this signal has a magnetic anisotropy. When studying the temperature dependence of EPR signals, in the behavior of such parameters as the amplitude of the magnetic resonance signal, the width of the magnetic resonance line, the formation of a characteristic Vervey phase transition at a temperature of 120-125 K, was found. The results were confirmed by the Messabauer method.

Conclusion

EPR spectroscopy has revealed the formation of new magnetic properties in biological systems as a result of stress factors. It was found that the process of biomineralization plays a role in the formation of biogenic iron oxide magnetic nanoparticles in plants, the generation of magnetite crystals in biological tissues, and stress factors have a stimulating effect on this effect. The effect of stress factors can be used in the biosynthesis of functional iron oxide nanoparticles applied in various fields. Detection of iron oxide nanoparticles by EPR signals can be used as a source of new biochemical and biophysical information in biomedical research. It was found that these nanoparticles have significant role in the functioning of living organisms and pathological situations. Experiments with EPR spectroscopy show that this method is a very promising way to detect the formation of paramagnetic centers in biological systems and to assess the environment.

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