Redox state of plastoquinone Q_A and photochemical electron transfer in photosystem II reaction centers

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Photosystem II is the source of O_2 in the atmosphere, one of the main targets of various stress factors in oxygenic organisms. This complex converts light energy into electrochemical energy with very high efficiency (≥98%). Therefore, it is very important to clarify the energetic and kinetic properties of the processes in its reaction centers. The paper is dealing with the effect of the redox state of plastoquinone (Q_A) acceptor on the quantum yield of the primary photochemical reaction in the PSII reaction center. For this purpose, Q_A was reduced by one or two electrons in an anaerobic medium, and the temperature dependence of the intensity of chlorophyll fluorescence was studied. Analysis of the results obtained in this study showed that the energy difference between P_{680}*Phe$Q_A^{\bullet-}$ and P_{680}Phe$Q_A^{\bullet-}$ states of the PSII reaction center is ~0.06 eV. This indicates that the effect of Q_A^{-} on the energetics and kinetics of photochemical electron transfer in the reaction center of PSII may differ from the effect of Q_A^{2-} on these reactions.

Keywords: *Photosystem II, plastoquinone, pheophytin, electron transfer, charge recombination*

Abbreviations:
Chl – chlorophyll; CP43, CP47 – 43 kDa and 47 kDa PSII core antenna proteins; D_1, D_2 – PSII reaction center proteins; F_0, F_M, F_V – initial, maximum and variable fluorescence of Chl; Q_A – plastoquinone, primary electron acceptor of PSII, $Q_A^{\bullet-}$ (semiquinone) reduced form; Q_B – plastoquinone, secondary electron acceptor of PSII; Phe – pheophytin, $Phe^{\bullet-}$ reduced form; P_{680} – primary electron donor, P_{680}* and $P_{680}^{\bullet+}$ excited and oxidized forms; PSII – photosystem II; RC – reaction center; Y_Z, Y_D – redox-active tyrosines of PSII.

INTRODUCTION

Photosystem II (PSII), the energy-converting multiprotein system of the thylakoid membrane of oxygenic photosynthetic organisms – plants, algae, and cyanobacteria, couples the photochemical excitation of chlorophyll with the electron transfer from water to plastoquinone (Vinyard et al., 2013; Shen, 2015; Shevela et al., 2023). It consists of approximately 20 protein subunits and a large number of cofactors involved in the capture of light quanta and excitation energy transfer to its photochemical reaction center (RC), and photochemical electron transfer across the thylakoid membrane mediated by photoactive chlorophyll molecule. The most important protein subunits involved in the PSII complex of plants are transmembrane D_1 (PsbA) and D_2 (PsbD) proteins, α- and β-subunits of cytochrome b_{559} (PsbE and PsbF, respectively), Chl *a* binding core antenna proteins CP47 (PsbB) and CP43 (PsbC), and three peripheral proteins of 33-, 23- and 17 kDa (PsbO, P, and Q, respectively) located on the lumen surface of thylakoid membranes. In cyanobacteria and red algae, PsbP and PsbQ polypeptides are replaced by the cytochrome c_{550} (PsbV) and 12 kDa PsbU polypeptides (Zouni et al., 2001; Ferreira et al., 2004; Umena et al., 2011, Ago et al., 2016).

Heterodimer of D_1 and D_2 proteins of PSII binds a photoactive chlorophyll molecule P_{680} (primary electron donor), pheophytin (Phe) as primary acceptor, and two plastoquinone molecules (plastoquinone O_A and Q_B) serving as terminal electron acceptors, two redox-active tyrosines Y_Z (D_1-Tyr^{161}) and Y_D (D_2-Tyr^{161}) as an electron donor (Muh and Zouni, 20114; Shen, 2015; Shevela et al., 2023). When P_{680} is excited, an electron transfer occurs to the pheophytin molecule for ~3 ps, resulting in the formation of oxidized $P_{680}^{\bullet+}$ and reduced $Phe^{\bullet-}$ radicals in the PSII reaction center (Klimov et al., 1977; Vinyard et al., 2013). The quantum yield of the $P_{680}^{\bullet+}Phe^{\bullet-}$ radical pair formation is approximately 0.98 (Groot et al., 1997). From $Phe^{\bullet-}$ the electron is transferred sequentially to plastoquinone Q_A and Q_B in ~250 ps and ~100 μs, respectively (Nuijs et al., 1986;

Bowes and Crofts, 1980; Robinson and Crofts, 1983; De Wijn and van Gorkom, 2001). Whereas Q_A is considered a one-electron carrier, Q_B can accept two electrons and two protons in succession. Protonated Q_B (Q_BH_2) is subsequently exchanged with neutral plastoquinone from the intramembrane plastoquinone pool, which serves as a reservoir for plastoquinols leaving PSII (Chen et al., 2019; Shevela et al., 2023). The oxidized primary donor, $P_{680}^{\bullet+}$ is a strong oxidant (E_m ~ 1.2 V) which is reduced by an electron from tyrosine Y_Z, and finally, oxidized tyrosine ($Y_Z^{\bullet+}$) is reduced by an electron from water (Muh and Zouni, 2011; Vinyard et al., 2013; Shen, 2015).

Plastoquinone Q_A located on the stromal side of the thylakoid membrane has a substantial role in electron transfer in the PSII reaction center and regulation of its energetic and kinetic properties (van Mieghem et al., 1989; 1992; Klevanik et al., 1991). This occurs due to a change in its redox state in a photochemical reaction (Ishikita and Knapp, 2005; Havaux, 2020; Leverne and Krieger-Liszkay, 2021). It is generally accepted that when Q_A is uncharged (state $P_{680}PheQ_A$), the PSII reaction center is “open” and the photochemical electron transfer there occurs with very high efficiency. This state is characterized by low intensity of PSII chlorophyll fluorescence denoted as F_0, which is often referred to as constant (as well as initial, fast) fluorescence of chlorophyll.

When plastoquinone Q_A is reduced photochemically by exposure of PSII to strong light, or chemically in the presence of a reducing agent such as dithionite (state $P_{680}PheQ_A^{\bullet-}$), the reaction center is said to be "closed", and this, in turn, reduces the efficiency of charge separation and electron transfer in the reaction center (Sipka et al., 2021). The reduction of plastoquinone Q_A causes a 4-5 fold increase in the yield of chlorophyll fluorescence from the level of F_0 to the maximum, denoted as F_M. One of the mechanisms proposed to explain the increase in the intensity of chlorophyll fluorescence was a model assuming a decrease in the efficiency of charge separation (electron transfer) and the inability of RC to use the excitation energy in a closed state (Duysens and Sweers, 1963; Kitajima and Butler, 1975). However, this interpretation has contradictions and is not enough to explain the molecular mechanism of the process. Another more attractive model ignores the closure of the RC and assumes that electron transfer occurs with high efficiency even during the reduction of Q_A, and the increase in chlorophyll fluorescence (variable fluorescence) considers the emission of luminescence as a result of the re-excitation of chlorophyll during charge recombination in the $P_{680}^{\bullet+}Phe^{\bullet-}$ pair (Klimov and Krasnovskii, 1981; Klevanik et al., 1991; Feyziyev, 2019).

The validity of the proposed model can be verified by studying the temperature and magnetic field dependencies of the fluorescence yield. According to the model, due to the presence of an energy barrier between the $P_{680}^{\bullet+}Phe^{\bullet-}$ and P_{680}* states, the fluorescence yield should exhibit a temperature dependence. In a photochemical reaction, single and double reduction of plastoquinone Q_A is possible, and it is possible that two different states of plastoquinone have different effects on the RC energetics (Klevanik et al., 1991; van Mieghem et al., 1995; Hillmann et al., 1995). When plastoquinone is double reduced, using the temperature dependence of the maximum fluorescence of chlorophyll, the energy barrier between the states $P_{680}^{\bullet+}Phe^{\bullet-}$ and P_{680}* was found to be ~0.12 eV (Klevanik et al., 1991; Feyziyev, 2019). Due to the lack of appropriate temperature curves of fluorescence in the Q_A^- state, the activation energy between the $P_{680}^{\bullet+}Phe^{\bullet-}$ and P_{680}* states was not estimated directly.

In this study, changing the relative content of $Q_A^{\bullet-}$ and Q_A^{2-} states of plastoquinone by illumination of PSII samples in anaerobic conditions, we determined the energy difference between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ on the basis of the temperature dependence of the maximum fluorescence of chlorophyll. This allowed us to estimate the energy gap between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and P_{680}* indirectly.

MATERIALS AND METHODS

Fragments of thylakoid membranes enriched with PSII reaction centers isolated from spinach chloroplasts after treatment with Triton X-100 were used in the studies (Berthold et al., 1981; Völker et al. 1985). The fluorescence measurements were carried out in the medium containing 25 mM HEPES (pH 7.5), 20 mM NaCl and 2 mM $MgCl_2$. In low-temperature measurements, 70% glycerol was added to the medium. Anaerobic conditions were achieved with the addition of glucose (15 mM), glucose oxidase (100 U/ml) and catalase (1000 U/ml) to the medium (Klimov et al., 1985). Photoinduced changes of chlorophyll fluorescence (constant, variable, and maximum fluorescence) were measured in a laboratory-built spectrometer equipped with an electromechanical modulator. The light intensity of ~5 μmol photon·m^{-2}·s^{-1} and wavelength 490 nm was used for the monitoring (excitation) of fluorescence. The intensity of λ>650 nm wavelength light exited photochemical electron

transfer in RC (actinic light) was ~1000 μmol photon·m^{-2}·s^{-1}. Low-temperature measurements were carried out in the same set-up, equipped with a laboratory-built cryostat, which allows measurements in the temperature range of 300 K–77 K. The temperature of the samples was controlled using a copper-constantan thermocouple immersed in the sample. The concentration of chlorophyll in the samples was 5 μg/ml.

RESULTS AND DISCUSSION

The energy of light quanta absorbed by antenna pigments initiates electron transfer in the PSII reaction center. The quantum yield of primary reactions is high and reaches up to the value of ≥ 98%. However, a small part of the energy absorbed by the pigments is not used usefully in the electron transfer process and is lost in the form of fluorescence emission. At room temperature, PSII chlorophyll fluorescence is maximum at 685 nm (Baker, 2008). The intensity of PSII chlorophyll fluorescence depends on the redox state of its reaction center components. In the uncharged state of the Q_A acceptor, the intensity of chlorophyll fluorescence is low (F_0), however, due to the reduction of plastoquinone, the fluorescence intensity increases to the maximum value of F_M, where $F_V=F_M–F_0$ is called variable fluorescence (Fig. 1*a*).

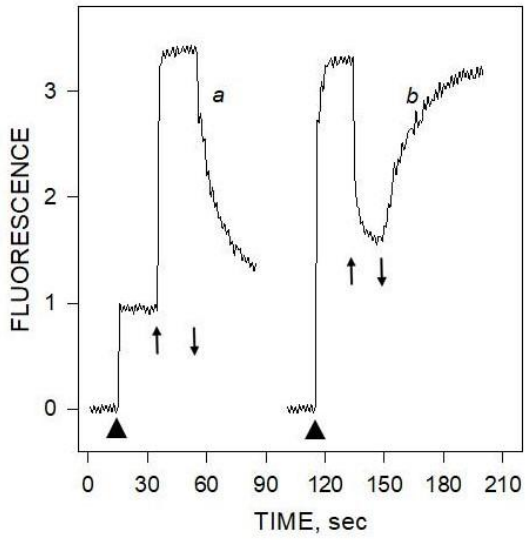

Fig. 1. Photoinduced changes of chlorophyll fluorescence under aerobic (*a*) and anaerobic (*b*) conditions: ▲ – measuring light (~5 μmol foton $m^{-2}s^{-1}$) on; ↑(↓) – actinic light (~1000 μmol foton $m^{-2}s^{-1}$) on (of). Concentration of chlorophyll in the samples was 20 μg/ml.

Reduction of plastoquinone in the PSII reaction center is possible photochemically under strong illumination (Fig.1*a*), chemically by adding electron donors, such as sodium dithionite, and creating an anaerobic environment using the glucose-glucose oxidase-catalase enzyme system. When using an enzyme system, a weak measuring light causes an increase in the fluorescence intensity. On the contrary, turning a strong actinic light causes a decrease in fluorescence intensity (due to photoreduction of pheophytin in the reaction center) which increased again when the active light was turned off (Fig.1*b*) (Klimov et al., 1985). It can be assumed that in this case, plastoquinone is reduced a second time (Q_A^{2-}) since the illuminated preparations differed from the non-illuminated samples in terms of the temperature and magnetic field dependence of fluorescence (Klevanik et al., 1991).

Using the data obtained from the temperature dependence of the fluorescence intensity in samples exposed to strong actinic light illumination, the energy barrier between $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ and P_{680}* states was estimated to be ~0.12 eV (Klevanik et al., 1991), while the energy gap between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and P_{680}* remained undefined. We used a pre-illumination procedure at a temperature range of 300 K-160 K for the preparation of samples at different states of QA under anaerobic conditions, achieved by adding glucose (15 mM), glucose oxidase (100 U/ml), and catalase (1000 U/ml) to the reaction medium. We assumed that illumination at high temperatures promotes the double reduction of Q_A, while low temperatures prevent this process, and most PSII centers still remain in the state $P_{680}PheQ_A^{\bullet-}$. After pre-illumination (for 1 min) and a brief dark relaxation (for 3 min) at the same temperature, the samples in the cryostat were cooled to 160 K, and then the intensity of chlorophyll fluorescence was measured when the samples were heated. The results of the measurement are shown in Figure 2. As seen from the figure, samples exposed to illumination at 300 K demonstrate a low intensity of chlorophyll fluorescence at low temperatures. The intensity of fluorescence growths with the increasing temperature up to 300 K, which is consistent with the results of the early studies (Klevanik et al., 1991).

In the samples exposed to illumination at temperatures of 270 K and 240 K, an increase in the fluorescence intensity with the temperature rise was also observed, although this dependence was less pronounced than was observed in the sample pre-illuminated at 300 K. However, samples illuminated at 200 K and 160 K showed different results. In such samples, a decrease in the intensity of PSII chlorophyll fluorescence was observed when the samples were heated. The temperature dependences of chlorophyll fluorescence intensity

observed in samples illuminated at 200 K and 160 K were similar to the temperature dependences of fluorescence observed in a sample that was not exposed to actinic light, which indicates the resemblance of the state of the PSII reaction center in such samples.

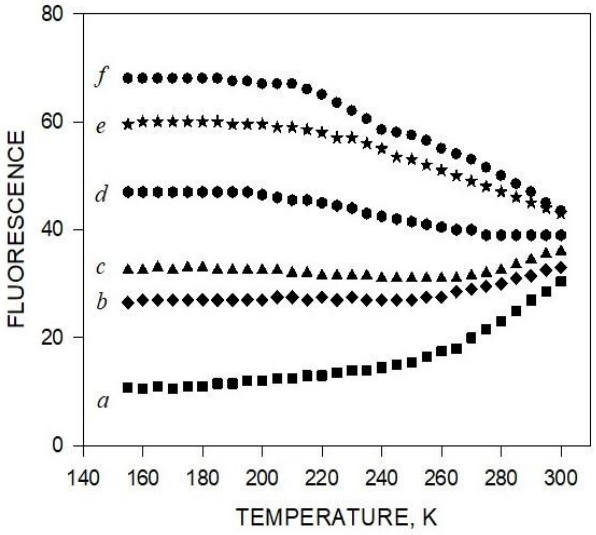

Fig. 2. Temperature dependence of the maximum fluorescence of PSII chlorophyll under anaerobic conditions. The PSII samples were illuminated with strong actinic light (λ>650 nm, ~1000 μmol photon·m^{-2}·s^{-1}) for 1 min at different temperatures: *a* – 300 K, *b* – 270 K, *c* – 240 K, *d* – 200 K, *e* – 160 K, f – non-illuminated sample. After keeping the samples in the dark for 3 min (for dark relaxation of fluorescence), the samples were cooled to 160 K, after which the fluorescence was recorded when the samples were heated. The light intensity of ~5 μmol photon·m^{-2}·s^{-1} and wavelength 490 nm was used for the excitation of fluorescence.

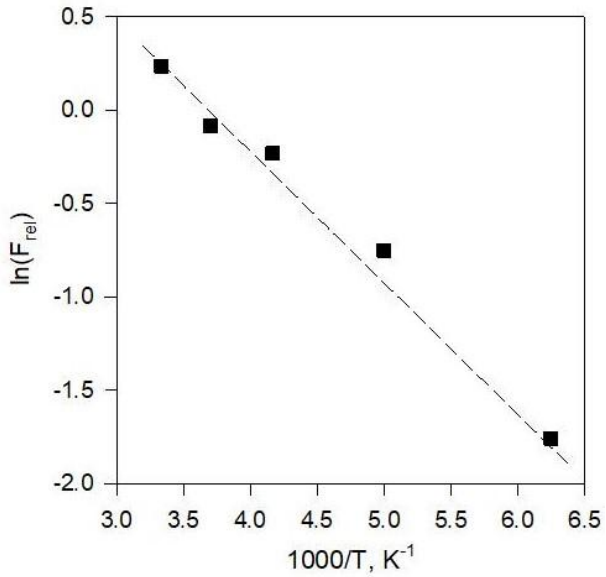

Fig. 3. Relative chlorophyll fluorescence after reduction of plastoquinone Q_A in PSII reaction centers are shown in Arrhenius coordinates.

Figure 3 represents an Arrhenius plot for the intensities of chlorophyll fluorescence demonstrated in Fig. 2, where the ordinate in the graph represents the relative change in fluorescence intensities observed at 200 K. Analysis of the graph shows activation energy of ~0.6 eV. This value of the activation energy likely corresponds to the energy barrier between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ and $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ that appeared in PSII reaction centers when they were illuminated at different temperatures. Thus, taking into account the value of the activation energy between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ and P_{680}* equals ~0.12 eV (Klevanik et al., 1991), we can assume that the value of the energy gap between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and P_{680}* is equal to ~0.6 eV.

When the plastoquinone Q_A is oxidized, the PSII reaction centers are believed in an "open" state, which favors photochemical electron transfer with a high quantum yield. A weak fluorescence of antenna chlorophyll, often referred to as an “initial” (also, “constant” or “prompt”) fluorescence can be observed in this state under weak measuring light preventing the accumulation of Q_A in the reduced state. However, during a photochemical reaction, a reduction of Q_A and an increase in fluorescence intensity of PSII chlorophyll to maximum (F_M) occurs, where $F_V=F_M–F_0$ is the variable fluorescence of chlorophyll. Unlike F_0, fluorescence in the presence of reduced plastoquinone $Q_A^{\bullet-}$ (F_V) is represented by luminescence resulting from the recombination of charge of the $P_{680}^{\bullet+}Phe^{\bullet-}$ pair (Klimov and Krasnovskii, 1981; Klevanik et al., 1991) and can be used as a tool in the study of the efficiency of photochemical reactions.

In this study, we have shown that the redox state of plastoquinone Q_A can tune the energetic properties of the PSII reaction center. In turn, this can lead to a change in the kinetic characteristics and the quantum yield of the primary photochemical reaction in PSII reaction centers. These results were obtained by measuring PSII fluorescence in two different putative states of plastoquinone obtained by illumination of PSII preparations in an anabolic environment at different temperatures. We assumed that these states of the reaction center as an electron acceptor have singly and doubly reduced plastoquinones.

The results of our study showed different temperature courses of the yield of maximum fluorescence of PSII chlorophyll, depending on sample pre-illumination temperature. The state established in the RC when illuminating PSII samples under anaerobic conditions at the temperature of 300K, we attributed to the state $P_{680}PheQ_A^{2-}$ of the reaction center. According to

earlier studies (Klevanik et al., 1991), as well as our studies, the activation energy between the $P_{680}PheQ_A^{2-}$ and P_{680}* states is ~0.12 eV.

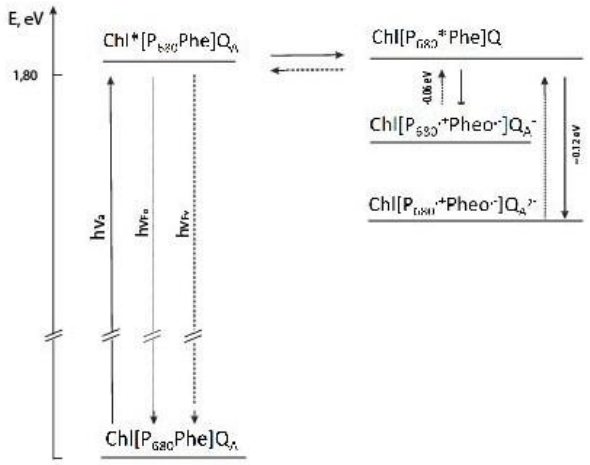

Fig. 4. The energy diagram for charge separation and recombination in the PSII reaction centers

In samples pre-illuminated at lower temperatures (< 240 K) and presumably in the state $P_{680}PheQ_A^{\bullet-}$ of the reaction center, the change in the intensity of chlorophyll fluorescence with decreasing temperature shows results different from the samples illuminated at higher temperatures. This dependence of the intensity of fluorescence on temperature does not allow us to determine the energy of the state $P_{680}PheQ_A^{\bullet-}$ and thus, the activation energy between the states $P_{680}PheQ_A^{\bullet-}$ and P_{680}*. However, an activation energy of ~0.06 eV, determined indirectly using the fluorescence intensities at 200 K, indicates that the energy of the state $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ is very close to the state P_{680}*$PheQ_A^{\bullet-}$, which has an energy of ~1.81 eV at 685 nm.

Due to such relatively small activation energy, the predominance of the equilibrium between $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and P_{680}* over the equilibrium between the states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ and P_{680}* seems to be possible. Due to such a relatively small activation energy, the equilibrium between $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{\bullet-}$ and P_{680}*, compared to the equilibrium between states $P_{680}^{\bullet+}Phe^{\bullet-}Q_A^{2-}$ and P_{680}*, can shift towards P_{680}*, which in turn can lead to a decrease in the efficiency of photochemical electron transfer in the PSII reaction center.

CONCLUSION

Among the components of the photosynthetic apparatus, PSII is the most sensitive to extreme factors, and therefore, the characteristic reactions of PSII including the electron transfer in its RC and fluorescence of chlorophyll *a* are attracted to researchers as indicating the physiological state of oxygenic species. In this sense, determining the relationship between the electron transfer and the intensity of chlorophyll fluorescence in photosystem 2 RCs is of particular importance. In this study, we tried to answer this question indirectly and showed that the redox state of plastoquinone affects electron transfer in RCs. However, a complete clarification of the problem requires more direct investigations.

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Plastoxinon (Q_A) elektron akseptorunun redoks halı və fotosistem II reaksiya mərkəzində fotokimyəvi elektron daşınması

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Fotosistem II (FSII) atmosferdəki O_2-nin mənbəyi, müxtəlif stress faktorlarının bitkilərdə əsas hədəflərindən biri, herbisidlərin birləşmə saytıdır. Bu kompleks işıq enerjisini çox yüksək effektivliklə (≥98%) elektrokimyəvi enerjiyə çevirir. Ona görə də onun reaksiya mərkəzlərində baş verən proseslərin energetik və kinetik xassələrinin aydınlaşdırılması çox əhəmiyyətlidir. Bu işdə FS II kompleksinin reduksiya olunmuş plastoxinon Q_A akseptorunun onun reaksiya mərkəzində ilkin fotokimyəvi reaksiyanın kvant çıxımına təsiri öyrənilmişdir. Bunun üçün anaerob mühitdə plastoxinon bir- və ya ikielektronlu reduksiya edilərək, xlorofilin maksimum fluoressensiyasının intensivliyinin temperaturdan asılılığı öyrənilmişdir. Alınmış nəticələrin analizi reaksiya mərkəzinin P_{680}*$PheQ_A^{\bullet-}$ və $P_{680}PheQ_A^{\bullet-}$ halları arasında enerji fərqinin ~0.06 eV olduğu göstərilmişdir. Bu göstərir ki, reduksiya olunmuş $Q_A^{\bullet-}$-nın PSII-nin reaksiya mərkəzində fotokimyəvi elektron daşınmasının energetik və kinetik xassələrinə təsiri Q_A^{2-}-nın bu reaksiyalara təsirindən fərqlənməsi mümkündür.

Açar sözlər: *Fotosistem II, plastoxinon, feofitin, elektron daşınması, yüklərin rekombinasiyası*