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Mathematical model for the analytical signal of an herbicide sensor based on the reaction centre of *Rhodobacter sphaeroides*

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Abstract

This paper introduces a mathematical model which makes it possible both to determine the concentration of photosynthetic herbicides and to obtain a quantitative parameter in order to compare their activity using a previously described sensing system. The working principle involves the changes in absorption properties at 860 nm of the reaction centre (RC) isolated from the bacteria *Rhodobacter sphaeroides* when photosynthetic herbicides are present. The method has been used for the determination and activity comparison of five photosynthetic herbicides: diuron, atrazine, terbutryn, terbuthylazine and simazine. Detection limits obtained were 2.2, 0.75, 0.046, 0.25, and 1.4 μM, respectively. The resulting order for the different herbicides according to their action on RC was: terbutryn > terbuthylazine > atrazine > simazine > diuron.
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1. Introduction

Approximately 10% of all plant species are weeds, and some of these cause serious economic losses in crop production. For this reason, herbicides (chemicals designed specifically to kill weeds) account for an important percentage of all pesticide sales [1].

The first chemicals used in weed control were inorganic compounds. Brine and a mixture of salt and ashes were both used by the Romans to sterilize the soil as early as biblical times. Some of the inorganic herbicides used during the last century were copper sulphate, sodium arsenite, arsenic trioxide, ammonium sulfamate, sodium tetraborate, sodium borate and sodium chlorate. Several of these are still useful in weed and brush control, but are rapidly being replaced by organic herbicides.

Herbicides can kill weeds by means of different actions. Of these, the most important are growth regulation, amino acid synthesis inhibition, lipid synthesis inhibition, seedling growth inhibition, photosynthesis inhibition, cell membrane disruption, and pigment inhibition. About one half of the herbicides used at present in agriculture inhibit photosynthesis, mostly by targeting the photosystem II complex. Based on the chemical structure and binding properties, most of these herbicides act by competing with natural plastoquinone for the binding place in the D1 protein (located in the reaction centre of the photosystem II) and by avoiding photosynthetic electron transport [2]. Photosynthesis inhibitors include the following herbicide families: triazines, phenylureas, uracils, benzothiadiazoles and nitriles.

Herbicides can be highly toxic for human and animal health, and the enormous increase in the application of herbi-

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cides in agriculture during recent decades has resulted in the herbicide pollution of both soil and water. Traditionally, high performance liquid chromatography and gas chromatography have been used to detect trace quantities of pesticides in water [3–5]. However, while chromatographic techniques allow high sensitivity herbicide detection, they also require expensive equipment, organic solvents, and the prior purification of the sample. This implies a limitation on the number of samples that can be analysed and the impossibility of using them as rapid screening methods. Different attempts have been made to introduce biological detection systems in order to overcome these problems. Several immunoassays have been developed, mainly enzyme-linked immunosorbent assays (ELISAs) [6–8] and immunosensors [9–12]. Most of them involve monoclonal antibodies which are specific to one or a few compounds having a similar chemical structure. Recently, an optical immunosensor able to detect several pesticides at the same time by using different fluorescent labels for each specific antibody has been described [13]. Other detection systems (mainly biosensors) for photosystem II herbicides that imitate the natural way of action of those herbicides have also been proposed [14–19]. Unlike ELISA methods, photosystem based sensors are not selective, but make it possible to determine all the compounds that affect a light-induced electron flow.

Some authors have proposed using the isolated photosynthetic reaction centre (RC) of purple bacteria, mainly *Rhodobacter sphaeroides*, as an optical transducer for the detection of photosystem II herbicides [20–24]. Due to the simplicity of material preparation (cultivation, extraction and purification), the purple bacterial RCs may be regarded superior materials to the photosynthetic proteins of plants for the development of herbicide detectors [23].

RC is a trans-membrane protein complex in which small organic cofactors are responsible for photon absorption and the subsequent electron transfer (Fig. 1). These cofactors are arranged along two almost symmetrical branches.

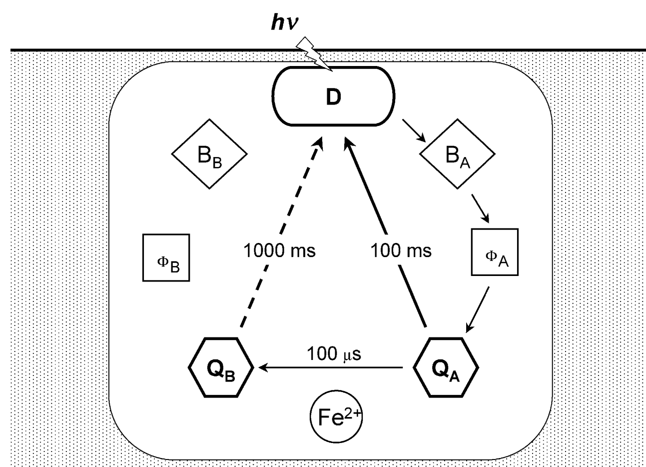

Fig. 1. Electron transfer processes between cofactors of the RC of *Rhodobacter sphaeroides* after light excitation.

However, the electron transfer is restricted to only one branch because of the structural engineering and specific environmental effects [25]. In substance, the absorption of a photon promotes a bacteriochlorophyll dimer (D) to its excited state. Consequently, an electron is transferred very rapidly, through a molecule of bacteriochlorophyll (B_A) and a molecule of bacteriopheophytin (Φ_A), to the first ubiquinone (Q_A), which is located in a hydrophobic pocket of the protein [20]. The electron is then rapidly transferred (about 100 μs) from Q_A to a secondary ubiquinone molecule (Q_B), which is located in a relatively polar protein domain. The return to the stationary state takes place at a charge recombination rate of about 1000 ms (dashed arrow). Moreover, Q_B is loosely bound to its pocket, and can be displaced from its binding site by competitive inhibitors, such as herbicides. If the Q_B binding site is empty or occupied by herbicides, the only possible recombination path is directly from Q_A (solid arrow), with a lifetime of about 100 ms.

The absorption spectrum of the RC complex shows different absorption bands corresponding to the different cofactors. The bacteriochlorophyll dimer contributes with a band at 860 nm that has the characteristic of being less intense for the excited form than for the fundamental state of the protein. Therefore, by following recombination kinetics by means of absorption at 860 nm, it is possible to learn the availability of the secondary ubiquinone and, consequently, the concentration of herbicides, since these can replace the latter ubiquinone.

In general, excitation of the RC is carried out with a flash lamp or a laser, and the subsequent 'time-resolved' absorption is then monitored [20,21]. Jockers et al. [22] describe a measuring method in which recombination processes are initiated and followed by continuous irradiation with weak actinic light.

Also in a previous work reported by the authors, simultaneous excitation and time-resolved absorption measurement are used by employing a light-emitting diode [24]: the development of the sensing system is described, with special emphasis on the design of the optoelectronic system which makes it possible to monitor the temporal changes in absorption following optical excitation.

The already described new sensing system [24] has been used in the present work for an in-depth analysis of the behaviour of the RC complex in the presence of different herbicides. According to the different published works based on RC as an optical transducer for the detection of photosystem II herbicides, the most original and relevant contribution to this work is the introduction of a mathematical model which makes it possible both to determine herbicide concentration and to obtain a quantitative parameter in order to compare the activity of different photosynthetic herbicides. This model has been validated by using standard solutions of five photosynthetic herbicides: diuron, atrazine, terbutryn, terbuthylazine, and simazine.

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