# Electron Transfer Modelling for the Effect of Magnetic Fields on the Photosynthesis Microalgae Enzyme (*Nonnochloropsis Salina*)

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*Abstract-* A mathematical modeling is applied to illuminate and predict the mechanism of electron transfer in algae photosynthesis. A magnetic field can accelerate its reaction by decreasing the frequency of reverse reactions in the radical pair mechanism. The effect of magnetic field (MF) changes the rotational dynamic of the radical pair and in general alters the yield and lifetimes of its product. The external magnetic field applied to the system causes a radical pair reaction change. This phenomenon can be explained by a rate constant $K_3$ for dual-reaction coordinate movement or triplet state formulation and according to the effect of the function rate dependent on magnetic $K_{ISC}$. To achieve a desired magnetic effect on the system, state that the of $K_3$ and $K_{ISC}$ rates must be equally large to observe the effect of the magnetic field on the reaction rate. In systems with forward reaction rate at $K_3 >> K_{ISC}$, the modeling result indicates that the maximum rate of effectiveness, $f(K_{ISC})$ is likely to occur at ≈7.85 militesla with ($K_{ISC}$) value at $2.63 \times 10^{-10}$ second. As simulated into the system, the MF influences reach at peak values of between 7.25mT ($6.24 \times 10^{-9}$ second, reaction rate) to 8.25mT ($3.94 \times 10^{-10}$ second, reaction rate). The significant result of the MF influences towards the microalgae growth production is indicated the range of $1 \times 10^{-10}$ to 7.75 militesla is observed to have influence on the rate of $f(K_{ISC})$.

*Index Terms-* mathematical modeling, influence, accelerate, convert, energy reaction, effect, transfer, absorb.

## I. INTRODUCTION

In algae photosynthesis, lights are transferred into chemical energy via photo induced electron transfer reaction. The whole process consists two consecutive: Light and dark phase. The light reactions include light absorption, transfer of excitons, and electron and proton translocation resulting in the production of NADPH2, ATP, and oxygen. In the light phase, a photochemical process occurs, transforming the photon energy of solar radiation into chemical energy. At first, the energy of the radiation is converted into the energy of the excited electrons, which is converted by oxidoreductase to macroergic compounds - ATP (adenosine triphosphate, source of chemical energy) and NADPH (nicotinamide adenine dinucleotide phosphate, reducing agent). The light reaction is due to the photosynthetic apparatus experiences sequences reaction as refer to photoreceptors that contain radiation-absorbing pigments, photosynthetic reaction center, where light energy is converted into electrical energy (= electron excitation by absorbed radiation) and string oxidoreductase, where excited electrons are converted to chemical energy (formation of ATP and NADPH) [1].

The reaction centre itself is composed of the two intrinsic polypeptides D1 (psbA) and D2 (psbD). D1 and D2 form a heterodimer and bind a variety of photochemical components such as chlorophyll P680, pheophytin, tyrosine YZ, and plastoquinone

QA and QB. The photosynthesis process starts with the excitation of the chlorophyll-a molecule pair P680. The excited of P680 molecule pair transfers an electron to another photochemical   Pheophytin . This electron is subsequently captured by the pheophytin as the primary electron acceptor. Four chlorophyll molecules and two pheophytin molecules are arranged into two branches associated with proteins D1 and D2 and located in the central part of the enzyme. The quinone acceptor complex of PS2 consists of two plastoquinone molecules with significantly different properties. The primary (QA) and secondary (QB) quinone acceptors function as one- and two-electron carriers, respectively as series of  electron then is move to  the plastoquinone QA, which is reduced to Q- A. The electron moves via plastoquinone is to be believe one of the radical pair mechanism in algae photosynthesis. The subsequent reoxidation occurs via another plastoquinone, QB, followed by taking up two protons as plastohydroquinol PQH2, transports the electrons to the cytochrome b6 / f complex ,A new plastoquinone QB from the so-called plastoquinone pool .
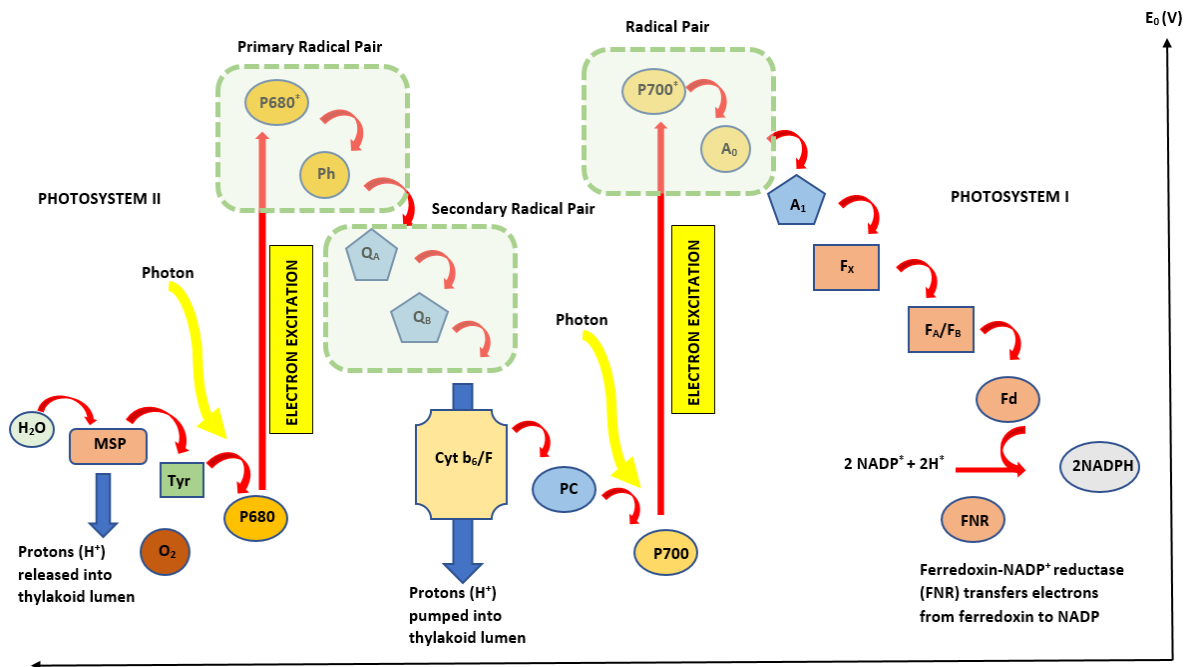


**Figure 1**: Z-scheme of the photosynthetic electron transport chain with a primary Radical pair mechanism that effected with the magnetic influences state as RP1, RP2 and RP3.

**Figure 1** shows that the axis on the left side of the diagram indicates the energy with respect to the redox potential $E_m$ at pH 7. After photon absorption, the reaction centers of photosystem II (P680) and photosystem I (P700) each change to the excited state P680 * and P700 *, respectively. P680 * gives an electron to the pheo- oxidizing side of the PSII, the oxidized P680 is reduced by tyrosine Z (Tyr, YZ). YZ phytin (Pheo), which is then forwarded to the plastoquinones QA and QB. In turn, its electrons are obtained from the manganese complex, which in turn removes them from the water [Whitmarsh and Govindjee, 2001].

The photosynthesis process starts with the excitation of the chlorophyll-a molecule pair P680. In most cases, the excitation energy is provided by an exciton transfer from the adjacent antenna complexes. The excited.The reaction center itself is composed of the two intrinsic polypeptides D1 (psbA) and D2 (psbD). D1 and D2 form a heterodimer and bind a variety of photochemical components such as chlorophyll P680, pheophytin, tyrosine YZ, and plastoquinones QA and QB [Richter, 1996]. P680 * transfers an electron to pheophytin a within 3 ps. From there the elec tron is passed on to the plastoquinone QA after 300-500 ps, resulting in Q⁻A reduced becomes. The subsequent reoxidation occurs via another plastoquinone, QB, which, in contrast to QA, can pick up a second

electron after renewed excitation before it then carries the electrons to the cytochrome b6 / f complex after taking up two protons as plastohydroquinol PQH2. A new plasma quinone QB from the so-called plastoquinone pool moves to the vacated area [Kern and Renger, 2007]

## II.    Electron Transfer Model

Electron Transfer Model (ETM) is reflected to photosystem within the photosynthesis system unit (PSU) that is defined as the reaction scheme from the effect of magnetic field (MF) as represented in Figure 2.
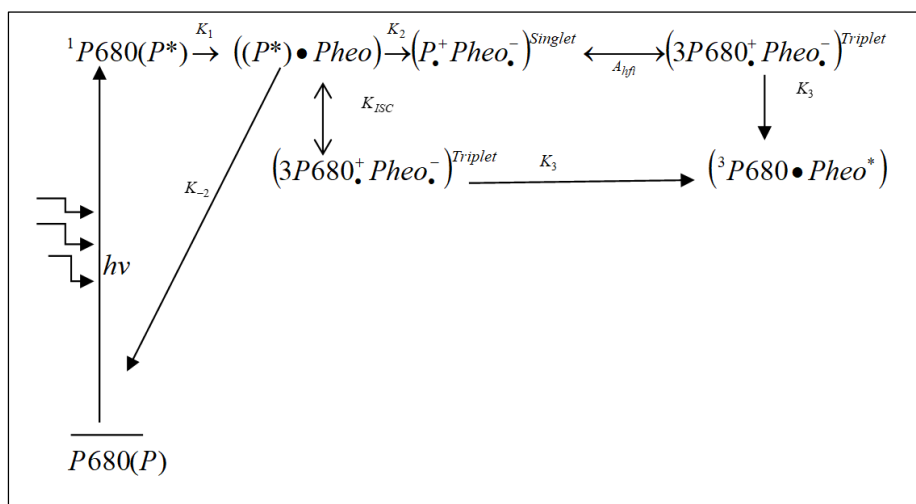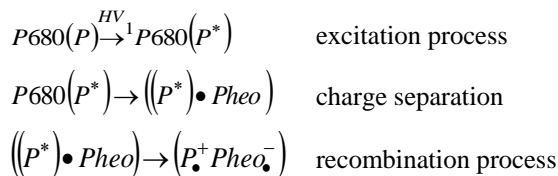


**Figure 2.** Photosystem unit (PSU) with magnetic effect radical pair mechanism.

The electron affinity of the acceptor molecules is increased upon the excitation with the effect of external MF. This is due to its collision with the donor molecule, Pheo. P* reduces a pheophytin *a* molecule Pheo within a few nanoseconds to form the radical pair state, $P^+Pheo^-$. For these processes, there are however two (2) possibilities in which either the singlet ground state ($P^+.Pheo^-$) or the triplet excited state of the acceptor ($3P680^+Pheo^-$) are produced.

**Figure 2** demonstrates the schematic diagram of the primary excitation, charge separation and recombination processes in the reaction center through P680 and Pheopytin which can be written as follows:

$$P680(P) \xrightarrow{HV} {}^1P680(P^*) \qquad \text{excitation process}$$

$$P680(P^*) \rightarrow ((P^*) \bullet Pheo) \qquad \text{charge separation}$$

$$((P^*) \bullet Pheo) \rightarrow (P_{\bullet}^+ Pheo_{\bullet}^-) \qquad \text{recombination process}$$

## III.    Coherent and Stochastic Motion

The state obtained depends on the relative alignment of the two unpaired electron spins of the electron back-transfer: singlet alignment leads to the singlet ground state and triplet alignment to the triplet state." The recombination (i.e. electron back-transfer) takes place over two (2) different time periods. A slow homogeneous recombination occurs after separation of the initially formed radical ion pairs" [1]. "Because of the small concentration of the initial pairs, the radicals must be diffused for about 10 ns" [2] "before they encounter other free radical ions with subsequent electron transfer. In this random encounter of radicals, the electron back-transfer produces result in singlet and triplet products. Since the relative orientation of the electron spins of 2A⁻ and 2D⁺ is

random, one has a 25% probability for singlet and a 75% probability for triplet alignments. The application of MF affects the spin dynamics of a radical pair and changes its product yields and lifetimes. MF can speed up a reaction by decreasing the frequency of reverse reactions" [3].

Coherent and stochastic motion in electron spin leads to interaction such as spin-orbit, exchange and hyperfine or Zeeman interaction in radical. The introducing of external magnetic field to radical at steady state gives a significant effect to the electron spin motion and triplet-singlet recombination product. "An analysis of the hyperfine coupling-induced recombination yields and their MF modulation furnishes valuable information about the existence of a short-lived radical pair and its microscopic diffusion in a solvent-mediated force field and about the reaction propensities to form singlet and triplet products" [1][4].

## IV.  Model Development Michaelis-Menten Kinetics

The MF introduced to the system influences the radical pair effect at ion exchange generation through $k_2$, a modified Michaelis-Menten kinetics with MF-dependent reaction rate are derived as in Eq. (1).

$$V^{mag}{}_m = \frac{K_4}{1 + \left(\frac{K_4}{K_2}\right)\left(1 + \left(K_2 + \frac{K_{-2}}{f(K_{ISC})}\right)/K_3\right)}[E_{TOTAL}]$$

(1)

Where, $V^{mag}{}_m$ is the maximum substrate concentration, $E_{(TOTAL)}$ is the total enzyme concentration. Furthermore, $K^{mag}{}_m$ is defined as constant rate of reaction in which the influences of MF is given in Eq. (2).

$$K^{mag}{}_m = \frac{\left(K_4/K_2\right)\left\{(K_1) + (K_2)\left(\frac{K_{-2}/f(K_{ISC})}{K_3}\right)\right\}}{1 + \left(K_4/K_2\right)\left\{1 + K_2 + \left(K_{-2}/f(K_{ISC})\right)/K_3\right\}}$$

(2)

Where, $K_{ISC}$ represents the influence of MF for the modified effective rate constant of radical pair recombination, $K_{-2}$. Reaction rate at $K_{ISC}$ is treated as a monotonic function $f(K_{ISC}): K_{-2} \rightarrow K_{-2} * ISC$, which leads to $K_{-2}/f(K_{ISC})$ as a new form of reaction rate at radical pair recombination with the influences of MF as shown in Eq. (3).

$$f(K_{ISC}) = \frac{2K_{ISC} + K_3}{K_{ISC} + K_3}$$

(3)

The probability of radical pairs recombination is given by $P_{ISC}$.  Thus, the influences of magnetic in radical pairs to determine the probability of singlet and triplet formation as in Eq. (4).

$$V^P = K_2\left(\left[{}^1AD\right](1 - p_{ISC})\right)$$

(4)

The rate of radical pair formation is represented as $K_2\left[{}^1AD\right]$. Further assumption is made as referring to the model radical pair recombination [11] with assumption made by [12], [13] which is assumed that the radicals are separated after a certain period of time and subsequent re-encounters are neglected.
The probability of radical pair recombination under steady state is given in Eq. (5).

$$p_{ISC} = \frac{K_{-2}/f(K_{ISC})}{K_{-2}/f(K_{ISC}) + K_3}$$

(5)

Numerical values of $K_2$ and $K_{ISC}$ are estimated from numerical and literature experimental studies. The recombination of radical pair is typically occurring at the range of $10^9 s^{-1}$. The initial spin correlation is removed at a lower range with the rates of $10^6 - 10^8 s^{-1}$ due to the electron spin relaxation processes. Intersystem crossing is induced by the hyperfine interaction mechanism that

occurs at the comparable rates in which the typical values of the hyperfine coupling constant are between 1mT to 10mT which is equivalent in between $0.2 \times 10^9$ to $2.0 \times 10^9$ rad/s. Finally, the $\Delta g$ mechanism can also lead to intersystem crossing rates exceeding $10^8$ - $10^9$ s$^{-1}$. C. [10] for example utilizing the $\Delta g$ value as $0.25 \times 10^{-8}$ s for the magnetic flux densities are in the range of 10mT to 100mT [11] and [10]. [14] have extended the probability equation for the rate dependent of magnetic effect at the rate of $K_{ISC}$ with the interaction and modification of hyperfine interaction constant (rad/s) with external MF. In their research publication hyperfine interaction, it is defined as Intra-radical coupling between the magnetic moment of an atomic nucleus and the magnetic moment of an unpaired electron, for zero MF, the rate of $K_{ISC}$ is represented Eq. (6).

$$K_{ISC}(0) = 3 \left( \frac{K_{-2} + 2K_3}{(K_{-2}/2 + K_3)^2 + (2J + a/2)^2} \right) \left( \frac{a}{4} \right)^2 \tag{6}$$

The equation is multiplied by the value of 3 due to an assumption made at zero value of MF. There are three (3) possibilities for singlet-triplet interconversion ($T_{-1}$, $T_{+1}$ and $T_0$) in the radical pair mechanism as the increasing of external MF in which the applied MF is greater than the hyperfine interaction, $B \gg A_{Hyperfine}$. Only one possibility channel remains $T_0$, in which this effect is due to the Zeeman interaction at $T_{-1}$ and $T_{+1}$ states that are energetically separated from the singlet-triplet interconversion states.

If MF is represented by $B$ that is assumed $B \gg A_{Hyperfine}$, then the rate can be defined as in Eq. (7).

$$K_{ISC}(B) = \left( \frac{K_{-2} + 2K_3}{(K_{-2}/2 + K_3)^2 + (2J)^2} \right) \bullet \left( \frac{(\Delta\omega)^2 + (a/4)^2 + \gamma \left[ (\Delta\omega)^2 - (a/4)^2 \right]^2}{1 + \gamma \left[ (\Delta\omega)^2 + (a/4)^2 \right]} \right) \tag{7}$$

in which,

$$\gamma = \frac{1}{K_3(K_{-2} + K_3)} \left( \frac{(K_{-2} + 2K_3)^2}{(K_{-2}/2 + K_3)^2 + (2J)^2} \right) \tag{8}$$

$$\Delta\omega = \Delta g \mu / (2h) \tag{9}$$

where,

| | | |
|---|---|---|
| $a$ | = | Hyperfine interaction constant (rad/s) |
| $J$ | = | Exchange interaction between the unpaired electron spin of the radicals' pair |
| $\Delta g$ | = | The difference between g-factors of two radical |
| $H$ | = | Reduced plank constant |
| $B$ | = | MF |

If, $J \approx 0$ and MF $\approx 0$ or MF is very weak, then $B \ll A$ and $\Delta\omega$ becomes negligible.

Martin Volk and Matthias Gilbert (1993) report that the determination rate in photosynthesis radical pair via high resolution MF-dependent measurements [6]. They investigate the comparison on the recombination rates of P680$^+$ Pheo$^-$ for photosystem II in photosynthesis within the temperature ranges from 90K to 300K. The results allow conclusion on the combination and recombination of radical pair in Photosystem II (PS II), Reaction center (RC), chlo-rophyl l (Ch-l), Pheophytin (Pheo), P680, primary donor in PS II, primary donor in algae photosynthesis and MF dependence of the reaction yields for S-T-mixing are singlet-triplet-mixing.

The external MF influences the photosystem which gives a significant effect for the triplet recombination channel, thus increases the radical pair lifetime[7]. This shows that both PS II and bacterial RCs of the singlet recombination rate is smaller than the triplet recombination rate. The singlet recombination rate in principle can be determined by the MF dependence at values of 0.002 ns at 90K and 0.01 ns at 290K are obtained with smaller than the values that is found in bacterial reaction centre[8].

The previous simulations result is gathered by employing the stochastic Liouville equation, MF modulation of the triplet yield and sensitivity of $K_{Singlet}$ indicate that rate of singlet formulation has values approximately at 0.0004 ns$^{-1}$ at 90K and 0.0015 ns$^{-1}$

at 290K. Furthermore, Trissl and Iavergne (1994) summarize the constant value of exciton radical pair model in their publication is continued by Bernd.M.A Kroons (2006) as shown in **Table 2.1**.

Table. 2.1: Literature constant value of exciton radical pair model.

| Constant | Value | Unit | Description |
|---|---|---|---|
| **Charge of recombination in PSII units with open centers** $(K_{\mathrm{Re}cm})$ | 0.3 | $ns^{-1}$ | The value of singlet and triplet recombination $(K_{-2} + K_3)$, [6] |
| **Reduction rate of quinone acceptor Q$_A$ (radical pair reduction)** | 2.3-4 | $ns^{-1}$ | Value of radical pair decay in PSU II open centre $(K_4)$, [6] |
| $K_3$ **represent bi-reaction coordinate motion / formulation of triplet state** | 30-60 | $ns^{-1}$ | *Martin Volk and Matthias Gilbert (1993)*[1] |
| $K_{-2}$ **formulation of singlet state** | 0.01 at 290K | $ns^{-1}$ | *Martin Volk and Matthias Gilbert (1993)*[1] |
| **Trapping constant for photosystem** $(K_1)$ **unit, depend on the chl a and chl b molecules** | $\dfrac{540}{chl_a + chl_b}$ | $ns^{-1}$ | *Radical pair model Tridsl and Lavergne 1994*[9][6] |
| **Rate** $K_2$ **Combination rate as of radical pair combination** | 4-6 | $ns^{-1}$ | *Chlorophyll triplet radical pair Alexander Angerhofer 1995*[10] |

## V.   Result and Discussion

The electron transfer mechanism continues to rise up until a certain maximal value represents the condition in which all the active sites in enzyme activity are filled with the appropriate substrate at a constant concentration of an enzyme in the PSU unit. Applying MF into the enzymatic system influences the formation of enzyme-substrate complexes as the rate of turn-over time is reduced and becomes the main factor in radical-pair mechanism affection as shown in Figure 3.
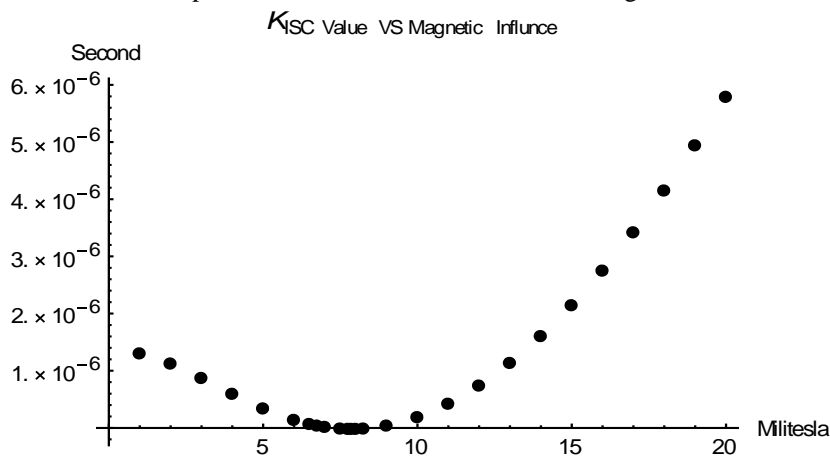


**Figure 3.** Simulation of MF effect on the Rate $K_{ISC}$ and on the growth probability of microalgae in a function of magnetic flux density, B (0-20 mT), (Eq. 7).

Microalgae productivity is the dependent rate in the determination of magnetic function. In order to achieve a desirable magnetic effect to the system, the rate excitation and respiration must be of similar magnitude to observe the effectiveness of MF on the reaction rate [10]. However, the effectiveness of MF against the singlet and triplet states (at photosynthesis) is always neglect able due to the short period of turnover time.

On the other hand, for the system with reaction with rate of short period of turnover time shows that the maximum rate of is likely to occur at approximately 7.85 mT at the range of $2.63 \times 10^{-10}$ second. The reaction rate per second show the influences of applied MF at range 5mT to 10mT, the reaction rate indicated a decreasing of reaction time from range of $1 \times 10^{-6}$ second to $1 \times 10^{-10}$ second with the increasing applied MF. However, the applied MF more than 9mT shows the increasing of reaction rate time as indicated the MF is no more having an influences of microalgae productivity. These simulation results give an insight that the applied MF decreasing the reaction time as the electron transfer mechanism likely to be accelerate.
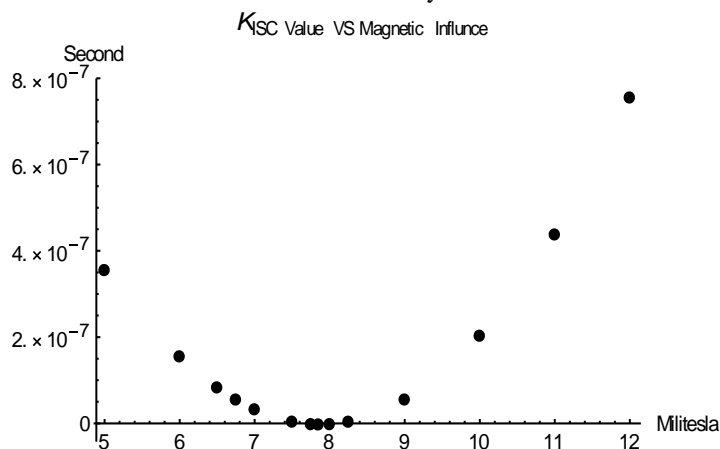


**Figure 4**. MF effect on the $K_{ISC}$, and on the radical pair mechanism in the reaction rate (in second) as a function of magnetic flux density, B (5-10 milli-Tesla),(Eq 7).
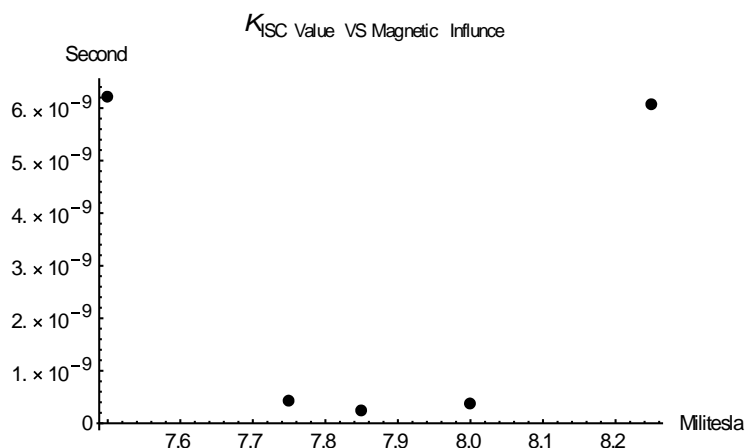
**Figure 5**. MF effect on the $K_{ISC}$, and on the radical pair mechanism in the reaction rate (in second) as a function of magnetic flux density, B (7.25-8.25 milli-Tesla), (Eq. 7).

The reaction rate, $K_{ISC}$ is treated as a monotonic function $f(K_{ISC}): K_{-2} \rightarrow K_{-2}/ISC$, which leads to the $K_{-2}/f(K_{ISC})$. The main reason for the function to be treated as monotonic is that as the influences of MF to the entire system, the magnetic effect can be assumed by either increasing or decreasing the rate constant of turnover time of radical pair formulation. From the simulation case, this function is assumed to have an increasing interval with the range of $1 < f(K_{ISC}) < 2$. The simulation results are plotted in Figure 6 and Figure 7.
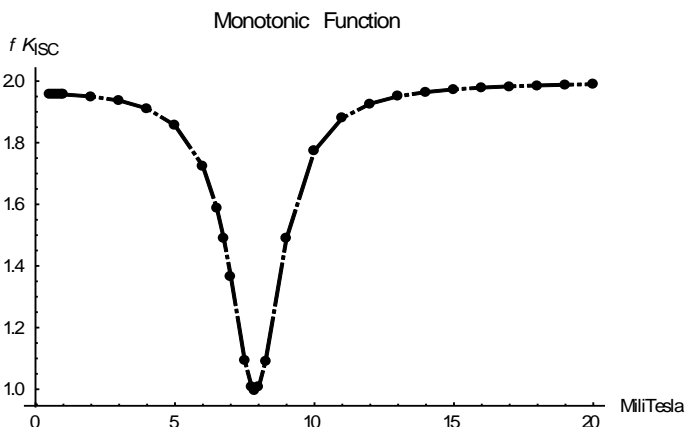


**Figure 6.** Monotonic function, (Eq.3), as the influences of MF to the entire system
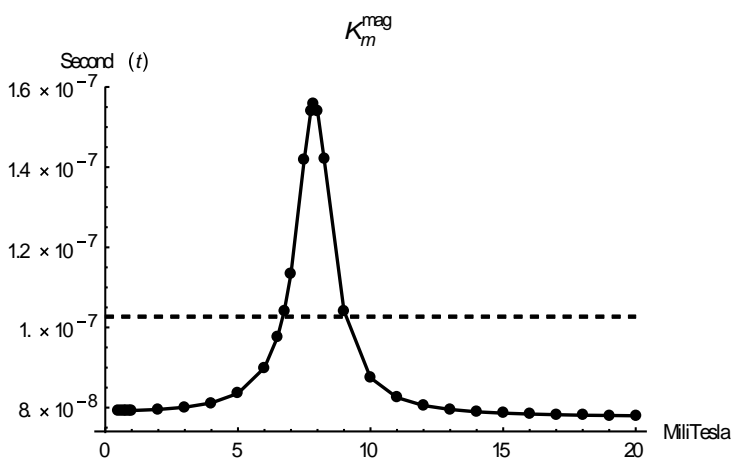


**Figure 7**. MF effect on the rate $K_m^{mag}$, represented as the rate of is defined as concentration of substrate at which the reaction speed is half of the $V_{MAX}$

Enzyme turnover number in the previous section is defined as the amount of substrate molecule that is converted into a product in an enzyme-catalyzed reaction. The MF influences the turnover number in algae photosynthesis enzyme activity which is depending on the rate-limiting step as it is represented in the previous section with the limited rate of $K_2$ (combination rate of radical pair) and $K_4$ (reduction rate of quinone acceptor $Q_A$). If the reaction rate is at $K_2 << K_4$ which is based on the radical pair theory [12], [13] and [20], the magnetic effect alters the maximum enzyme reaction rate as represented by $V_{max}^F$ as shown in Eq. (10).

$$\frac{V_{max}^F}{[E_{total}]} = \frac{K_2}{1 + (K_2 + K_{-2}/f(K_{ISC})/K_3)} \quad (10)$$

The turnover number of the enzyme can be calculated depending on whether the rate-limiting step in the enzyme cycle occurs before or after radical pair generation. If $K_2 << K_4$, then the result can be simulated as plotted in Figure 8.
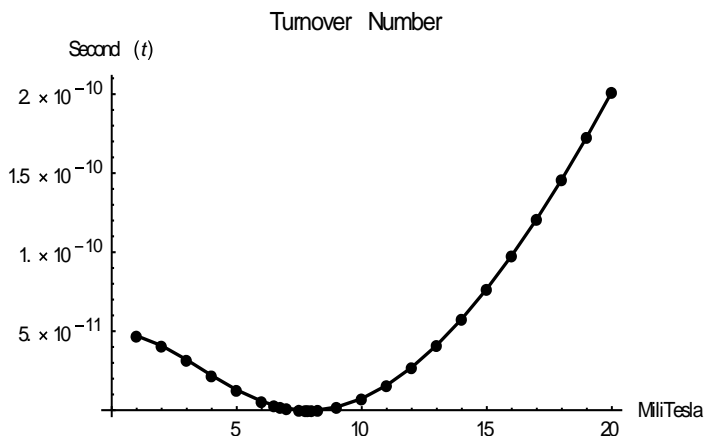


**Figure 8.** Simulation Result on enzyme turnover number in radical pair mechanism.

## VI. Conclusion

The mathematical modelling for the MF effectiveness of the electron transfer energy towards the algae photosynthesis is successfully developed and the simulation results are discussed. The rate of production of microalgae is determined by the effectiveness of the magnetic energy supplied. The MF influences is exerted on the recombination probability as the theorem derived from origin transition state theory focusing on radical pair mechanism that is generated within the photosystem unit PSU.

## Acknowledgments

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