



Electrochemical Harvesting of Photosynthetic Electrons from Unicellular Algae Population at the Preparative Scale by Using 2,6-dichlorobenzoquinone



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ABSTRACT

Oxygenic photosynthesis is the process used by plants, cyanobacteria or algae to convert the solar energy into a chemical one from the carbon dioxide reduction and water oxidation. In the past years, many strategies were implemented to take benefits from the overall low yield of this process to extract photosynthetic electrons and thus produce a sustainable photocurrent. In practice, electrochemical tools were involved and the principle of electrons harvestings was related to the step of electron transfer between the photosynthetic organism and a collecting electrode. In this context, works involving an algae population in suspension were rather scarce and rather focus on the grafting of the photosynthetic machinery at the electrode surface. Based on our previous works, we report here the implementation of an electrochemical set-up at the preparative scale to produce photocurrents. An algae suspension, i.e. an intact biological system to ensure culture and growth, was involved in presence of a centimeter-sized carbon gauze as the collecting electrode. The spectroelectrochemical cell contains 16 mL of suspension of a *Chlamydomonas reinhardtii* mutant with an appropriate mediator (2,6-DCBQ). Under these conditions, stable photocurrents were recorded over 1 h whose magnitude depends on the quinone concentration and the light illumination.

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1. Introduction

In the current context of renewable energies, sunlight is the most abundant and sustainable source of energy available on Earth [1–3]. This is why photosynthesis is now considered as one of the strategies to take benefits from the solar energy. Indeed, photosynthesis is the biological process involved by Nature to feed the biosphere with reduced carbon. However, it only uses a very small fraction from the sunlight energy (the overall yield is few % of the total energy available from sunlight being converted into chemical energy) [4], while the photochemical converters (Photosystems I and II) remain very efficient [5]. Among several limitations which lower this yield, a prominent saturation of the

photochemical conversion comes from the kinetic limiting transfer step located downstream of Photosystem II (see Fig. 1). Therefore, under high-light conditions, Photosystem II cannot fully release its charge. As a consequence, the overall yield is intrinsically decreased because PSII does not reach its maximal turnover rate. Furthermore, the PSII primary electron acceptors accumulation in their reduced state will lead to photoinhibition, that is the formation of reactive species which can damage the photosynthetic chain [6]. The cost associated with the sustained maintenance of the photosynthetic machinery (damage/repair cycles) also contribute to diminish the global yield. Paradoxically, the apparently disappointing performance of photosynthesis makes it a promising fuel-producing factory. Indeed, this saturation of the photochemical conversion while quantum efficiencies of photosystems remain excellent would suggest that photosynthesis is an unexploited reservoir to produce electricity by harvesting electrons among the photosynthetic chain under high-light conditions.

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¹ Fabrice Rappaport deceased before completion of this manuscript. His co-authors wish to dedicate this article to his memory.

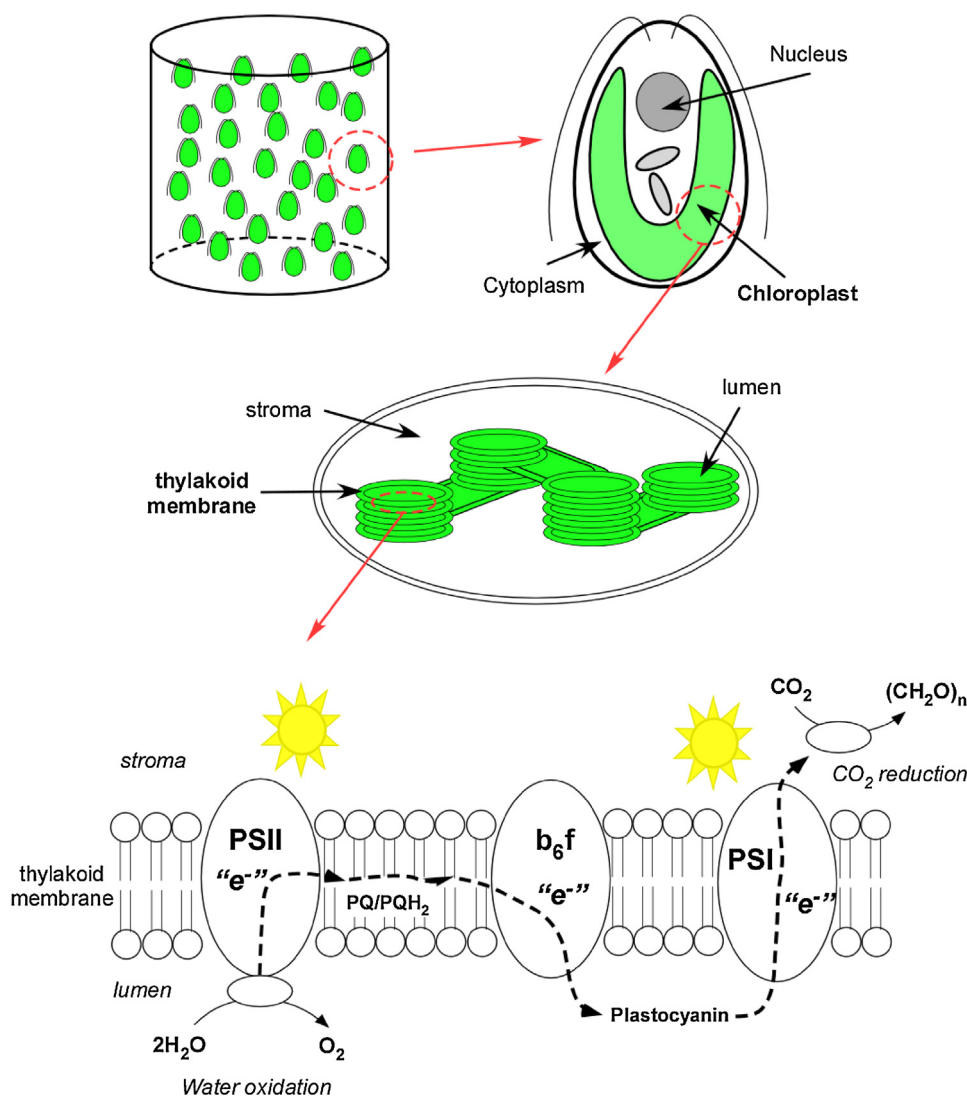


Fig. 1. Simplified schemes of the photosynthetic machinery considered in this work. A) Green unicellular alga population in suspension. B) Representation of the green algae *Chlamydomonas reinhardtii*. C) Scheme of a chloroplast containing thylakoid membranes. D) Photosynthetic chain within a thylakoid membrane. The dashed line traces the electron flow along from the PSII (water oxidation) to the final CO₂ reduction. In short, light absorption induces Photosystem II (PSII) excitation. One of the possible PSII deexcitation pathways occur through a charge separation that leads to water oxidation. Several subsequent steps involving the plastoquinone (PQ)/plastoquinol (PQH₂) pool, the cytochrome b₆f (b₆f) and the Photosystem I (PSI) eventually leads to and CO₂ reduction. The electron transfer rate determining step occurs between the PQ/PQH₂ pool and the b₆f complex.

In that way, recent strategies mainly involved a collecting electrode for harvesting the electrons from the photosynthetic organism though with different biological targets or electrochemical set-ups. For instance, benefits could be taken from the good efficiencies of photosystems by grafting isolated PSII or PSI on the electrode surface [7–11]. Using native photosynthetic membranes immobilized on the working electrode [12,13] also helps to avoid the step of biochemical purification of photosystems [14–18]. Moreover the electrical connectivity between the electrode and the photosynthetic unit can be enhanced by using redox polymers, nanotubes, nanoparticles or exogenous mediators. Finally, intact biological systems like cyanobacteria [19–23] or algae [24,25] can be considered. This is a more long lasting approach because it potentially ensures the culture and proliferation of the photosynthetic organisms during the electrons extraction. However, the electron harvesting is made more difficult because of a restricted access to the photosynthetic chain due to extra and intracellular membranes or other aqueous compartments to cross. This is

probably why works involving cell suspensions are often limited to the analytical level [26–28].

In that purpose, we demonstrated in the past the ability of several exogenous quinones (chloro, methyl and phenyl derivatives) to extract photosynthetic electrons from the green unicellular algae *Chlamydomonas reinhardtii* [29,30]. In the present work, we report the implementation of an electrochemical set-up aimed to use a suspension of a *Chlamydomonas reinhardtii* mutant at the preparative scale. An appropriate exogenous quinone will act as an electron carrier from the electrons harvesting to its re-oxidation at the collecting electrode surface. Photocurrents from 10 to 60 $\mu\text{A}\cdot\text{cm}^{-2}$ were effectively recorded, depending on the quinone concentration as well as the light illumination.

2. Experimental

2.1. Cell culture and preparation

Chlamydomonas reinhardtii $\Delta petA$ mutant was grown in Tris Acetate Phosphate medium (TAP) containing Tris base (20 mmol.L⁻¹), NH₄Cl (7 mmol.L⁻¹), MgSO₄ (0.83 mmol.L⁻¹), CaCl₂ (0.45 mmol.L⁻¹), K₂HPO₄ (1.65 mmol.L⁻¹), KH₂PO₄ (1.05 mmol.L⁻¹) at 25 °C under rather dim light conditions (50 $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) to a cell suspension at a concentration of 10⁷ cells.mL⁻¹, then centrifugated at 4000 tour.min⁻¹ and then re-suspended into PBS medium for electrochemical experiments (see below) to reach a final steady concentration of 10⁷ cells.mL⁻¹ that corresponds to stable conditions for algae.

2.2. Chemical materials and solutions preparation

All chemicals have been purchased from sigma Aldrich and have been used without any further purification. 2,6-DCBQ was dissolved in absolute ethanol in order to make mother concentrated solutions. Appropriate small volumes of such quinone solutions were thus directly added to the algae suspension for subsequent electrochemical experiments (see below).

2.3. Electrochemical experiments

2.3.1. Photocurrent recording

A home-made spectroelectrochemical cell was used (see Fig. 2). Experiments were achieved in TAP supplemented with PBS to reach an adapted ionic strength (~ 150 mmol.L⁻¹) for

electrochemical measurements. In practice, 7.4% of a concentrated PBS (6.66 times more concentrated than the one used for cyclic voltammetry, see **Supporting Information**) is added to the TAP medium described above. A carbon gauze (geometric area = 1 cm², Mersen, Courbevoie, France) was used as the working electrode, a platinum plate as the counter electrode, and an Ag/AgCl 1 mm diameter wire as the reference electrode. In order to perform chronoamperometric measurements at constant potential, the set-up corresponds to an adapted three-compartment cell by separating the counter electrode from the electrolysis medium with a fritted glass of medium porosity. All the measurements were carried out at 25 °C. The control of the applied potential value and the acquisition of the current-time curves were achieved by the mean of a QuadStat potentiostat supplemented with an e-corder data recorder (eDAQ).

Illumination was achieved by the mean of a JTS spectrophotometer (Biologic). The actinic (excitation) light was provided by a red LED (640 nm) at two incident lights (135 or 340 $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$).

Practically, after growth and centrifugation, the *Chlamydomonas reinhardtii* cells are re-suspended in PBS-TAP medium and 16 mL of solution (with an algae concentration of 10⁷ cells.mL⁻¹) are transferred in the spectroelectrochemical cell. In order to avoid sedimentation of the algae, the solution was stirred with an overhead stirrer (Ref: VOS 14, VWR international) at 100 r.p.m. The biased potential was set in darkness at 0.65 V vs. Ag/AgCl in absence of 2,6-DCBQ. The current was then recorded every 2 s. After stabilization of the baseline (needed to remove the high capacitive current resulting from the high electrode surface area), 2,6-DCBQ (previously dissolved in ethanol) is added to reach the given concentration (40; 75 or 100 $\mu\text{mol}\cdot\text{L}^{-1}$). A current increase

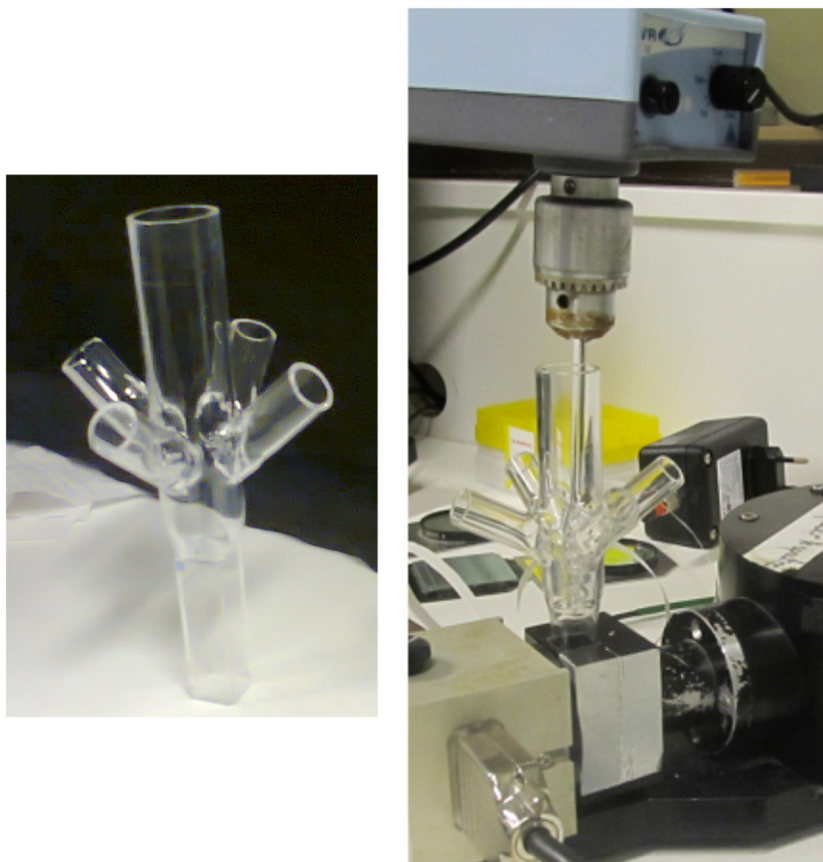


Fig. 2. Photograph of the set-up used in this work. Left: the spectroelectrochemical cell. The illumination zone is located at the bottom of the cell. Right: the whole set-up.

($\sim 10 \mu\text{A}$) thus appeared, probably due to the interaction between the quinones and the respiratory chain [29]. After a new stabilization of the baseline, illumination is performed during half an hour. The end of the recording only occurs when the current returned to the baseline. The variations of light-dependent current are obtained by fitting the baseline and subtracting it from the raw data.

3. Results and discussion

3.1. Implementation of the experimental set-up

Among various substituted quinones, 2,6-dichlorobenzoquinone (2,6-DCBQ) was previously demonstrated to be one of the best acceptors to extract photosynthetic electrons from PSII [29,30]. Assuming this harvesting leads to the hydroquinone form, electrochemistry is an appropriate tool to restore the active quinone form. As a consequence, using an efficient collecting electrode is needed for chronoamperometry experiments. It can be achieved if considering a high surface area electrode within the cell suspension solution. We thus considered a home-made spectroelectrochemical cell (see Fig. 2) with a centimeter sized (geometric size) carbon gauze as a working electrode. Its potential is poised at +650 mV vs Ag/AgCl in the experiments for ensuring the oxidation of the hydroquinone form (see **Supporting Information**). As a proof of concept, the algae considered in this work (as well as the light incident flows; see below) will be those already investigated in previous fluorescence measurements in order to establish consistent results with the intrinsic PSII acceptor ability of 2,6-DCBQ determined elsewhere [29]. This is why a mutant of *Chlamydomonas reinhardtii*, ΔpetA was involved (see Fig. 1) [31]. In this mutant, no significant light induced electron transfer can occur unless added quinones provide a way to specifically allow the electron harvesting (and thus the produced photocurrent from chronoamperometry experiments) directly from PSII.

3.2. Photocurrent recordings

Two representative experiments of photocurrent production are displayed in Fig. 3. The algae suspension is illuminated in presence of 2,6-DCBQ when a potential value of +650 mV vs Ag/

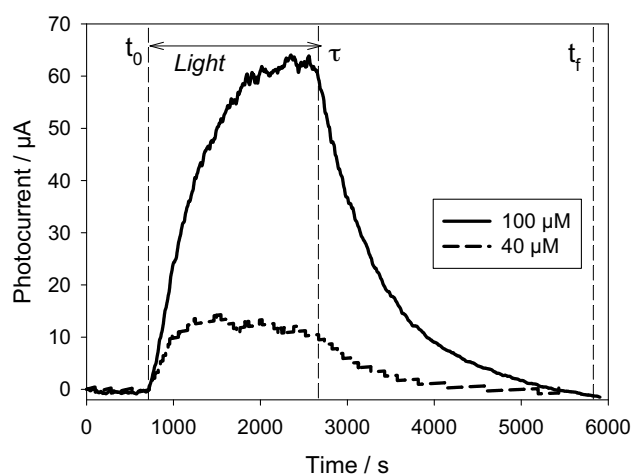


Fig. 3. Current recorded as a function of the time (after baseline subtraction) at the carbon surface ($E = 650 \text{ mV vs Ag/AgCl}$) from a suspension of *Chlamydomonas reinhardtii* ΔPetA mutants ($10^7 \text{ cells.mL}^{-1}$) in TAP (see experimental part) in presence of 2,6-DCBQ 40 μM (dashed line) and 100 μM (solid line). The period of illumination (incident light flow $340 \mu\text{E.m}^{-2}\text{s}^{-1}$) is indicated.

AgCl is applied at the carbon gauze collecting electrode. After switching on the light ($I^\circ = 340 \mu\text{E.m}^{-2}\text{s}^{-1}$), a current slowly increases as a function of the time until reaching a stationary value. The light-dependence of this current is evidenced by switching off the light. The corresponding decrease and return to the baseline demonstrates that the photocurrent is expectedly related to the harvesting of photosynthetic electrons by the exogenous 2,6-DCBQ and its renewal through an electrocatalytic cycle involving the collecting electrode. As evidenced in Fig. 3, the steady state photocurrent magnitude depends on the quinone concentration. The same trend is observed at lower light illumination (see Fig. S2 in SI). Globally, the dependences of the incident light flow and quinone concentration are summarized in Table 1 and show that the current densities recorded in this experimental configuration range from 5 to 60 $\mu\text{A.cm}^{-2}$. Such current densities are globally of the same order of magnitude as the other works aimed to harvest photosynthetic electrons while a more accurate comparison is prevented by the very different experimental conditions used in each strategy (with or without mediator, grafted photosynthetic organisms, entire photosynthetic organisms or subunits, illumination wavelength, light incident flow . . .). However, the reported photocurrents in our work correspond to a higher scale, i.e. at the preparative level. Moreover, it has to be emphasized that the photocurrents were more stable. Under illumination, the steady-state current is therefore stable over one hour and naturally returns to zero after 8 hours if illumination is constant during this period.

3.3. Effect of the 2,6-DCBQ concentration and incident light flow

The effects of 2,6-DCBQ concentration and light incident flow are depicted in Table 1 (and Fig. S3 in SI). As an example, the steady-state photocurrent value is reduced by 4–5 when the concentration varies from 100 to 40 $\mu\text{mol.L}^{-1}$. Such a strong decrease is consistent with the partition phenomenon previously evidenced [29]. Indeed cellular compartments (other than the thylakoid membrane where electron transfer occurs) may sequester a portion of the added quinones therefore preventing them to interfere with the thylakoid membrane. In the case of 2,6-DCBQ, the concentration of available quinones is about 20 $\mu\text{mol.L}^{-1}$ in saturation conditions. As a consequence, the effects of a quinone concentration decrease is amplified in terms of recorded current, especially for quinone concentrations close to the value at which the sequestering compartments are saturated. Furthermore, in our conditions, the photocurrent drastically decreases when the illumination is diminished from 340 to 135 $\mu\text{E.m}^{-2}\text{s}^{-1}$. This decrease ratio (~ 3) remains close to the incident light flow decrease ratio (~ 2.5). This observed dependence of the incident light flow on the photocurrent seems in agreement with an extraction phenomenon controlled by electronic harvesting efficiency rather than the re-oxidation at the electrode surface since only the first step kinetically depends on the incident light flow and the quinone concentration [30].

Table 1

Steady state photocurrent (in μA) values (related to the light illumination of the algae suspension) as a function of the 2,6-DCBQ and incident light flow.

$C (\mu\text{mol.L}^{-1})$	100	75	40
$I^\circ (\mu\text{E.m}^{-2}\text{s}^{-1})$			
340	60 ± 2	–	12 ± 1
135	20 ± 2	14 ± 2	5 ± 1

3.4. Photocurrent analysis

As evidenced above, the quinone and light dependence thus suggest a kinetic limitation by the quinone photoreduction by cells. This is confirmed by some basic calculations from the experimental currents. The area of the current-time curves (A_{curve}) can thus be compared to the measured steady state current (i_{ss}). As an example, the i_{ss} and A_{curve} values for $I^{\circ} = 340 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $C_{\text{Q}} = 100 \mu\text{mol}\cdot\text{L}^{-1}$ are $64 \mu\text{A}$ and 133mC respectively (illumination time $\tau = 1900\text{s}$). The A_{curve}/τ ratio is thus equal to 70 and close to the i_{ss} value. The real area during the current decrease (switching off the illumination at τ until the baseline return at t_{r} ; see Fig. 3) is measured as $A_{\text{decrease,exp}} = 0.0244C$. In the case of the rate limitation by the electrochemical oxidation, the concentration of the hydroquinone form in solution should be at most equal to $100 \mu\text{mol}\cdot\text{L}^{-1}$. Knowing the volume (16 mL) and the Faraday's law, the corresponding area during the decrease should be equal to $0.309C$, that is far from the experimental value. Such a result is confirmed by a more general trend in Fig. 4 which displayed a linear relationship between i_{ss} and A_{curve}/τ with a slope close to the unit ($y = 0.924x$; $R^2 = 0.9974$).

However, the kinetic limitation involved in the process seems more complicated to rationalize if estimating the extraction rate from the chronoamperograms and its comparison to expected values. For instance, with $I^{\circ} = 340 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and an introduced quinone concentration of $100 \mu\text{mol}\cdot\text{L}^{-1}$, i_{ss} is about $60 \mu\text{A}$, i.e. a global rate ($=i/F$) of about $620 \text{pmol}\cdot\text{s}^{-1}$ of electrons. With an incident light of $340 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, the photochemical rate ranges from 5 to 6 ms per PSII center, i.e. around $200 \text{photons}\cdot\text{s}^{-1}\cdot\text{PSII}^{-1}$. Under our conditions, the PSII concentration is close to $50 \text{nmol}\cdot\text{L}^{-1}$ and the light beam illuminates 1 mL of solution. The maximum biological rate can be estimated to $10 \text{nmol}\cdot\text{s}^{-1}$ of electrons. Moreover, the photosynthetic electrons extraction induced by exogenous quinone is not a quantitative process. The extraction yield $\Phi(I^{\circ}, C_{\text{Q}})$ is thus close to 0.55, leading to a global rate of $5.5 \text{nmol}\cdot\text{s}^{-1}$ [29,30]. Indeed, the experimental rate is finally equal to $0.62 \text{nmol}\cdot\text{s}^{-1}$, i.e. a lower value than the expected one with a unique kinetic control by the quinone extraction step. This suggests that other competitive phenomena (being not quite fast to be neglected) can play a role on the global rate. For instance, the different membranes in algae may slow down the diffusion of reduced quinones from the thylakoid to the electrode surface. Furthermore, a photosynthetic chain unstability may occur due to

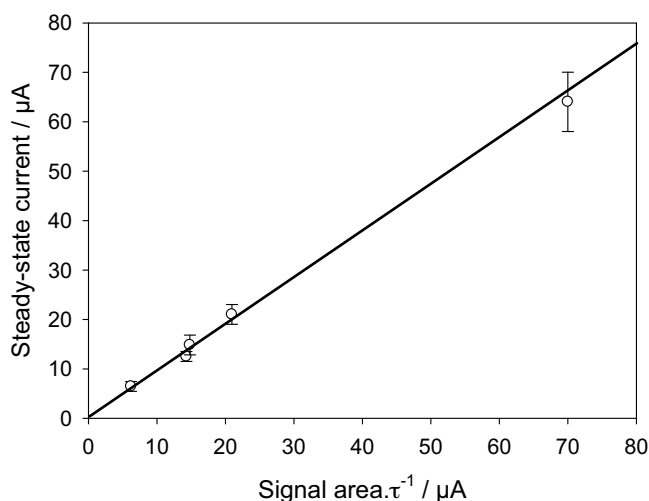


Fig. 4. Steady state current recorded during illumination with regard to the ratio between the area of the I-t curve and the illumination time ($t = 1900\text{s}$) for all the electrochemical experiments reported in this work with 2,6-DCBQ.

the light (photoinhibition) or quinones itself (toxicity) at long times.

4. Conclusion

In this work, we took benefits from previous experiments devoted to the interaction between exogenous quinones and the photosynthetic chain of green cellular algae. An electrochemical set-up was implemented at the preparative level (centimeter size carbon gauze, volume of 16 mL) to produce a photocurrent related to the extraction of electrons from PSII. The resulting current densities validate the strategy to work with algae suspension and contribute to recent works at the preparative scale [32,33]. Furthermore, under our experimental conditions, the process is probably controlled by the quinone extraction step while other competitive phenomena (diffusion within membranes, photoinhibition and even quinone decomposition at long times . . .) should be considered in future experiments for enhancing the extraction method in terms of current magnitude and stability over the illumination time.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2017.03.124>.

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