Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D

F. L. Souza[1], C. Saéz[2,*], J. Llanos[2], M. R. V. Lanza[1], P. Cañizares[2], M. A. Rodrigo[2]

[1] Institute of Chemistry of São Carlos, University of São Paulo, P.O. Box 780, 13560-970 São Carlos-SP, Brazil
[2] Chemical Engineering Department, University of Castilla-La Mancha, Edificio Enrique Costa Novella. Campus Universitario s/n, 13005 Ciudad Real, Spain

Abstract

In this work, the removal of a model pesticide (2,4-Dichlorophenoxyacetic acid, 2,4-D) using Electrokinetic Soil Flushing (EKSF) powered directly by DC current or by solar panels during a 15 days long treatment has been studied. Results show changes in operating conditions during the solar test, which can be clearly related to the day-night cycle, with a maximum solar irradiation intensity of 513 W m^{-2} at noon and an average daily charge supplied of 6.2 Ah d^{-1}. The fluctuations in the intensity supplied to the electrochemical system lead to softer pH and conductivity profiles between anodic and cathodic wells in the case of photovoltaic (PV) powered system. After the 15 days long tests, the removal of 2,4-D reaches 90.2 % and 73.6% in the electroremediation powered with DC power supply and solar panels, respectively. In this period,the total applied charge passed is 4.3 and 24.3 Ah kg^{-1} in both system, respectively. This means that the PV-powered electroremediation results in a much less efficient system, in which a much higher amount of charge is required to reach the same removal of pollutants in the soil. This fact may be related to the significantly lower EO flux observed during the operation of the PV-powered system.

Keywords: Solar energy, soil remediation, herbicide, photovoltaic, electrokinetic soil remediation.

*Corresponding author
Tel: (+34)902204100 ext. 6708
Fax: (+34)926295256
e-mail: cristina.saez@uclm.es

Highlights

- The average daily charge supplied during EKSF powered with solar panel is 6.2 Ah d^{-1}
- The pH profile between anodic and cathodic sides is softer in solar-driven processes.
- In solar-driven processes electromigration seems to be the most important remediation mechanisms.
- After 15 days, 90.2 % and 73.6% of 2,4-D removal were attained with EKSF powered with DC power supply and PV solar panels.

1. Introduction

During the recent years, an increasing interest in the electroremediation of soils with pesticides has appeared due to their excessive use in agricultural regions that can put at risk the quality of soil and water and have serious effects on drinking water reservoirs [1]. Among them, herbicide 2,4-dichlorophenoxy acetic acid (2,4-D) has been one of the most used pesticides [2] and, as a consequence of its high solubility and acidic properties it has become a serious problem of soil and groundwater contamination. In the recent years, its removal from surface or groundwater has been widely studied [3-14] and now the scientific effort is focused on its removal from soil and the design of strategies to control its diffusion into the soil.

In this context, the electrokinetic remediation could be a good alternative to contain and/or remove organic pollutants from soil. Electrokinetic soil flushing (EKSF) is carried out by the combination of processes that occur in the soil when a direct current (DC) is applied through electrodes placed into the soil. Among them, electrokinetic transport processes (electromigration, electrophoresis and electro-osmosis) favor the transport of pollutants and their removal from soil [15-18]. In order to enhance the performance of EKSF, recent studies have evaluated the influence of the electrode configuration, the electrode material and the addition of certain fluids to enhance the mobility of the pollutants. However, despite the high versatility of EKSF, the electrical energy consumption (around 10-15 % of the total cost [18], is a main barrier to applying this technology. In this context, powering soil eletroremediation with green energy is a challenge in the search for novel eco-friendly environmental remediation processes. In fact, in recent years the use of solar photovoltaic panels as an energy source for powering electrochemical systems has begun to be developed, and currently several works have focused on the use of renewable energy power sources to decrease both the investment and maintenance costs of electrokinetic remediation processes [19-23]. As known, power generation of solar panel depends on sunlight (that is, daytime and weather conditions) and thus it leads to significant energy fluctuations, and as a consequence the system becomes fed by a non-constant energy source. However, duration of remediation treatment is typically very long and due to the large time-constants coupling of a non-continuous supply should not have a negative impact on results. In fact, several works[20, 24-27] have reported that a pulsed EK process can enhance the removal of contaminants form soil and even decrease the electrical energy consumption and minimize the operation problems related to electrode corrosion. Likewise, recent studies [19-23] show that solar powered electrokinetic remediation drive the treatment of metals polluted soils with removal efficiency comparable with that achieved by DC power supply. However, many of the studies on solar-based EKSF were limited to short treatment periods in which it is difficult to evaluate correctly the advantages of using this energy source.

Thus, with this background, this work aims at studying the differences between the removal of a model pesticide (2,4-D) using EKSF powered directly with DC current or with the output of solar panels during a 15 days long treatment. To do this, two experiments at bench scale were run under the same operation conditions and main operation parameters were monitored and compared.

2. Materials and methods

2.1. Chemicals

Kaolinite provided by Manuel Riesgo Chemical Products (Madrid, Spain), was used as a model of clay soil. Kaolinite is not reactive and it has low hydraulic conductivity, low cation exchange capacity and no organic content, and for these reason it is frequently used as a model of low-permeability soils. Properties of this synthetic clay soil were provided by the commercial supplier, and are detailed in Table 1. All chemicals, including anhydrous sodium sulphate, sodium phosphate (Fluka, Spain), 2,4 dichlorophenoxyacetic acid (Sigma-Aldrich) were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 ºC) was used to prepare all solutions.

2.2. Electrokinetic bench-scale cell

Bench-scale setup was made of methacrylate and consists of an orthoedric tank divided into five compartments (Figure 1). The central compartment (with a total length of 20 cm) was loaded with herbicide-polluted soil, which was compacted manually and separated from the electrode compartments by a 0.5 mm nylon mesh. In one of these compartments it was placed the anode and in other the cathode. Graphite electrodes (10.0 cm × 10.0 cm × 1.0 cm), provided by Carbosystem (Madrid, Spain) were used as electrode material. Each electrode compartment was connected to an additional collector compartments to collect the liquid overflowing from the wells that is transported by the electrokinetic processes (electro-osmotic flow). In one of the experiments the EKSF cell was connected to a DC power supply while in the other to photovoltaic panels. Electricity produced by two photovoltaic plates connected in series (area of 1.313 m^2 each panel) can be used to power the electrochemical cell or it can be stored in batteries. Computer software (Labview, National Instruments) was used to control the process, and during the tests, energy was directly supplied to the electrochemical cells. The PV panels were located on the roof of the Environmental Engineering Laboratory (E3L) of the University of Castilla-la Mancha (38.59 N 3.55 O) and oriented to the south. The duration of the experiments was 15 days and they took place during January 2015.

To prepare the soil column, firstly, a pesticide solution containing 500 mg dm^{-3} of 2,4-D was prepared with tap water. This solution was used to pollute the soil, up to a 30% of the moisture. Then, herbicide-polluted soil was compacted manually in the central compartment of the cell. This compaction was done very carefully, in order to avoid the formation of heterogeneities in the soil that may result in preferential paths for the hydraulic fluid transport. Tap water was used as electrolyte in the soil and in the electrodic wells. The loses of water due to the evaporation process and also due to the electro-osmosis were replaced with the same electrolyte, added to the anodic well by means of a on/off regulation loop.

2.1. Analysis procedures

Daily, the electrical current, the temperature on different portions of the soil, the electro-osmotic volume removed from the cathode collector, pH, conductivity, pesticide and TOC concentration of the electro-osmotic fluid were monitored. The liquids contained in the electrolyte wells were also daily monitored measuring pH, conductivity and pesticide concentration. At the end of the experiment, a *post mortem* analysis was carried out to evaluate the final state of the treated soil and pH, conductivity, humidity and pesticide concentration were measured. For this analysis, the soil compartment was divided into sixteen pieces [28]. Sampling procedure of each point of the soil consists of taking it out carefully from the set up and manually homogenizing it. Once it was homogeneous, representative samples were taken for carrying out each analysis. Measurement of the moisture was carried out by drying the soil samples in an oven for 24 h at 105 ◦C. Moisture was calculated taking into account the weight difference in the samples before and after drying. For the determination of the pH and conductivity in the soil samples, the standard method of the saturated paste (E.P.A.-9045C, 1995) was used. This method consists of the mixture of 10 g of dry soil with 25 mL of distilled water which was magnetically agitated for 20 min. After sedimentation, the aqueous supernatant phase was prepared to analysis. All the samples (*pre and post mortem*) were filtered with 0.45 µm nylon filters from Whatman before their analysis. The decay of herbicides was followed by reversed-phase chromatography. The chromatography system was an Agilent 1100 series coupled a UV detector. The analytical column Phenomenex Gemini 5 µm C18 was used. Mobile phase consisted of 60 % acetonitrile and 40 % water to 2 % acetic acid with a flow rate of 0.4 cm^3 min^{-1}. The detection wavelength used was 280 nm. Temperature oven was maintained at 25 ºC and volume injection of 20 µL. Measurements of pH were carried out with an InoLab WTW pH-meter. Conductivity was measured using a Conductimeter GLP 31 (Crisol Instruments, Spain). The soil temperature was monitored using a Digital Soil thermometer (Spectrum Technologies, Inc.)

3. Results and discussion

3.1. Current profiles in electrokinetic system fed with PV panels.

Figure 2 shows profiles of the solar irradiation intensity and the resulting total current charge passed to the EKSF cell during the continuous 15 days-test in which the soil column was electrically powered by the set of two photovoltaic solar panels. These results aimed to show the main features of the electric powering of the EKSF system.

As expected, the solar irradiation profile (part a) was clearly related to the day-night cycles, with maximum solar irradiation values during the noon time slot and minimum values during the night. The changes in the climatologic conditions (with alternative sunny and cloudy days) explain the fluctuations in the maximum values (ranging from 275 to 513 W m^{-2}) attained day by day. Part b of the Figure shows the intensity powered to the EKSF cell. As shown, the solar irradiation profile clearly affects the current intensity supplied. Thus, the current intensity profiles follow almost the same trend, with maximum daily peaks of intensity ranging from 0.59 to 0.77 A and negligible current during nights. This pattern clearly reflects on the total current charge applied to the cell, which exhibits a marked stepwise trend. During the test, a total electric charge of 77.8 Ah was applied to the electrokinetic remediation reactor.

Figure 3 shows the average daily current intensity and applied charges during the fifteen days of testing. As can be observed, daily values exhibit deviations up to 30% with respect to the average value, which may be clearly related to the solar power irradiation profile (Figure 2a). However, even in the worst climatologic conditions (from days 7 to 12) the daily intensity and electrical charge supplied were above 0.2 A and 4.5 Ah. Likewise, these values indicate that the average daily charge supplied by this power source is 6.2 Ah d^{-1}, which taking into account the surface of the PV panels corresponds to 2.4 Ah d^{-1} m^{-2}

3.2. Electroremediation of soil powered by PV panels.

To evaluate the influence of the changing current produced by the PV powering system on the electrokinetic remediation of a soil polluted with 2,4-D, results of the EKSF powered by PV panels were compared with those obtained in a EKSF powered by a conventional power supply. In this latter case, the EKSF was driven potentiostatically (1 VDC cm^{-1}).

Figure 4 shows the changes in the current density applied between the electrodes during the two tests carried out: the reference experiment in which the electric field is kept constant (1 VDC cm^{-1}) by means of a DC power supply and the green powered EKSF, for which it was made the direct connection to the electrodes of two solar panels without the assistance of batteries. In the case of the conventional experiment, no daily profiles are produced during the day but just negligible random fluctuations, while in the case of the PV panels powered system, the profiles were periodic and significant as discussed in the previous section of this manuscript and they may have an important influence on performance and efficiency. As it can be observed in Part a, the average current density applied with the solar powered technology is higher and also dependent on the day. This trend opposites the behaviour observed for the ESKF test powered with DC power supply, in which a small decrease is observed during the progress of the test and lower average values are obtained.

Part b of the figure focuses on the changes in the temperature measured in a central point of the soil columns. As it can be seem, a soft decrease is observed in both EKSF tests, which was related more to the room temperature than to the electrochemical process. This observation suggests that ohmic loses are not important in these tests, in principle because of the low current applied. In this point, it is important also to take in mind that temperature is measured in the farthest point from the electrodes, that is, the point in which lower temperature profiles caused by ohmic loses are expected.

Because of the low influence of the ohmic loses on the process performance, the electrokinetic processes are expected to become the most important processes associated to the application of an electric field to soil. In particular, the transport of water by electro-osmosis (EO) is of interest because it may drag the pollutant from the soil. Figure 5 compares the electro-osmotic fluxes measured in both systems. Despite the higher applied current density in the system powered by the PV panels, the resulting EO flux is much higher in the conventionally DC powered system, suggesting that the extreme daily profiles of intensity are not good to promote a continuous flow of water. On the other hand, in comparing the values of the evaporation flows, it can be observed that daily values fluctuate importantly, which can be associated to the different environmental conditions affecting the process. However, the average values of the evaporation flux obtained in the two tests are comparable (0.041 vs 0.046 cm^3 cm^{-2} d^{-1} in the solar powered and conventionally powered systems, respectively).

As it has been described in the methodology section, after the tests a *postmortem* analysis was carried out to characterize the most relevant parameters and to obtain 3-D plots. As it can be observed, not great differences are obtained between both systems, with measured moistures in the range 25-30%. There is a higher moisture in the zones closed to the anode. This increase is observed in the two experiments and may be explained in terms of the continuous addition of water to anodic well to compensate the loses of water by EO flux to cathode well and by evaporation.

One of the most characteristic changes produced during electrochemically assisted remediation processes are the changes in the pH caused by the oxidation and reduction of water on the surface of the electrodes. Typically, these changes make that the catholyte become strongly alkaline while the anolyte acidic. In addition, pH of the soil undergoes important fluctuations with the well-known acidic and basic fronts caused by the transport of these ions. For the experiments carried out in this work, changes in the pH pare shown in Figure 6. As can be observed, the changes in the anode and cathode wells are well observed in the system powered by the electric power converter but they are not observed in the soil remediation powered with the PV panels, where there is no profile of pH in the wells or in the soils. To explain these strange results it should be taken into account that pH was not monitored in continuous mode but measurements of pH were made once per day and that the on-times and off-times during PV powered system contribute to abate the fluctuations of this parameter. This fact can help to explain the differences observed with the data reported in literature [19,22].

Changes in the values of pH should reflect on the value of conductivity in the soil (Figure 7). As expected, the abrupt pH profile observed in the soil after the treatment with conventional power supply is related to a higher conductivity of the soil, as compared to the solar-powered process for which a softer change is observed.

Another important parameter is the concentration of 2,4-D that still remained in the soil after the 15 days treatment tests. These results are shown in Figure 8. In the EKSF essay power with a DC devices, the zone close to cathodic wells is completely cleaned. This means that drag pesticide is mainly flushed from soil by the water flux created throughout the cell and thus the EO flux is the most relevant removal mechanism. Likewise, the higher concentration of 2,4-D in position 1 (the closest to the anodic well) can be explained by the contribution of 2,4-D electromigration. The acidic behaviour of 2,4-D ($pK_a = 2.64$), implies that this molecule is only present as a non-ionic form at strongly acidic pHs, behaving as anion in the typical range of pHs contained in the soil. Thus, 2,4-D can also be transported by electromigration towards the anode, increasing the concentration measured after the test in the portions of the soil closest to the anode.

After the 15 days long tests, the removal of 2,4-D reaches 90.2 % and 73.6% in the EKSF powered with DC power supply and solar panels, being the total applied charge passed 4.3 and y 24.3 Ah kg^{-1}, respectively. This means that the PV-powered EKSF results in a much less efficient system, in which a much higher amount of charge is required to reach the same removal of pollutants in the soil. This fact may be related to the significantly lower EO flux observed in the case of PV-powered system.

4. Conclusions

The following conclusions can be drawn from the results of this study:

- EKSF can be powered using PV solar panels. During the 15 days tested, the average daily charge supplied by this power source varies is 6.2 Ah d^{-1}.
- The electroremediation of a soil polluted with 2,4-D can be achieved when the system is directly powered by PV solar panels. The magnitude of the electrokinetic processes, mainly electro-osmosis flux, depend on the fluctuations in the current intensity applied at each moment.
- The pH profile between anodic and cathodic sides is softer in the system powered with the PV panels. In this case, the on-times and off-times can contribute to abate the changes of this parameter.

- After the 15 days long tests, it was possible to remove 90.2 % and 73.6% of 2,4-D in the electroremediation powered with DC power supply and PV solar panels, respectively. The worse results obtained with PV-powered system could be related to the lower electro-osmotic flux registered in this case and thus to the lower amount of 2,4-D drained in the cathode well. In solar-driven processes electromigration seems to be the most important remediation mechanisms.

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Table 1. Properties of kaolinite used as model of low permeable soil.

Mineralogy		**Particle size distribution (%)**	
Kaolinite	100.00%	Gravel	0
Fe_2O_3	0.58%	Sand	4
TiO_2	0.27%	Silt	18
CaO	0.10%	Clay	78
K_2O	0.75%	Specific gravity	2.6
SiO_2	52.35%	Hydraulic conductivity (cm/s)	1×10^{-8}
Al_2O_3	34.50%	Organic content (%)	0
Others	11.42%	pH	4.9

Figure Captions

Figure 1. a) Layout of the experimental setup. b) Sections of the soil for the post-mortem analysis**.**

Figure 2. Changes in the **a)** solar power irradiation intensity and **b)** applied current intensity and total current charge passed during the test.

Figure 3. Changes in the average daily applied current intensity (▲) and current charge passed (Δ) during the test.

Figure 4. Changes in the applied current density (part a) and temperature (part b) during the EKSF tests powered by PV panels (▲) and DC power supply (△)

Figure 5. Water management during the electroremediation tests powered by PV panels (full symbols) and DC power supply (empty symbols). a) Changes in the evaporation (■, ☐) and electro-osmotic fluxes (▲, △) b) . Moisture distribution in the soil after the 15 days remediation tests. Upper right position (●, ○), upper left position (■, □), bottom right position (♦, ◊) and bottom left position (▲, Δ).

Figure 6. Changes in the pH during the electroremediation tests powered by PV panels (full symbols) and DC power supply (empty symbols). a) time course of the pH in the catholyte well (■, ☐) and anolyte well (▲,△). b) pH map of the soil after the remediation tests. Upper right position (●, ○), upper left position (■, □), bottom right position (♦, ◊) and bottom left position (▲, △).

Figure 7. Conductivity map of the soil after the remediation tests powered by PV panels (full symbols) and DC power supply (empty symbols). Upper right position (●, ○), upper left position (■, □), bottom right position (♦, ◊) and bottom left position (▲, Δ).

Figure 8. 2,4-D pesticide map of the soil after the remediation tests powered by PV panels (full symbols) and DC power supply (empty symbols). Upper right position (●, ○), upper left position (■, □), bottom right position (♦, ◊) and bottom left position (▲, Δ).

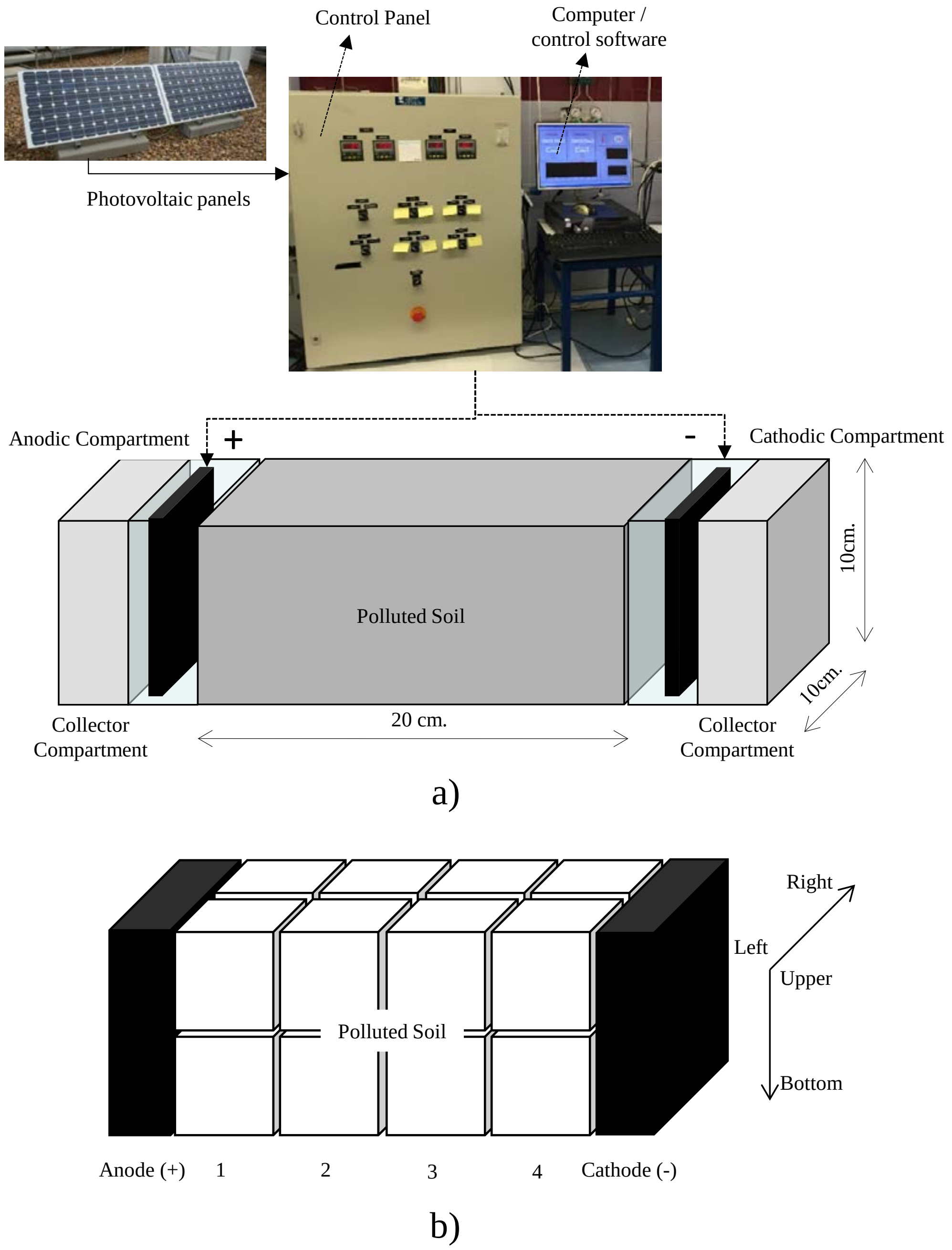
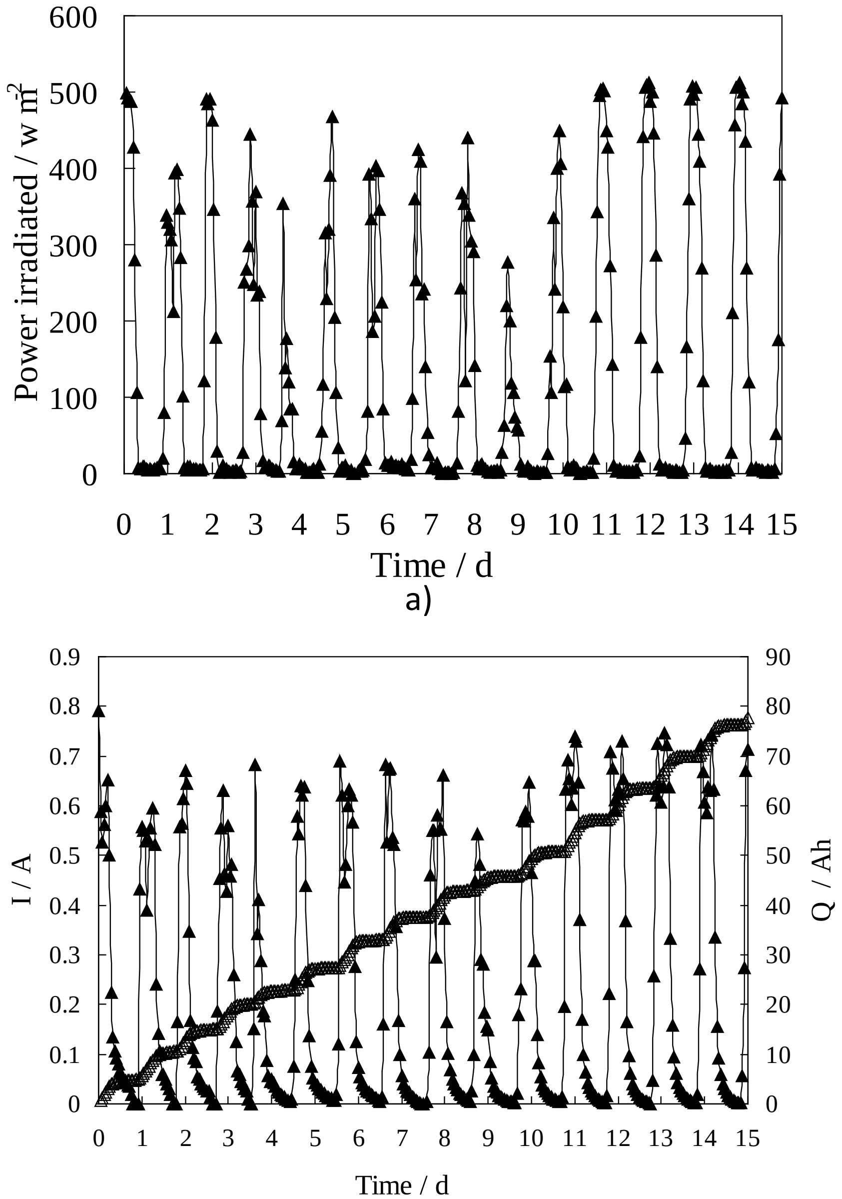

Control Panel
Computer / control software
Photovoltaic panels
Anodic Compartment
+
-
Cathodic Compartment
Polluted Soil
10cm.
10cm.
Collector Compartment
20 cm.
Collector Compartment
a)
Right
Left
Upper
Polluted Soil
Bottom
Anode (+)
1
2
3
4
Cathode (-)
b)

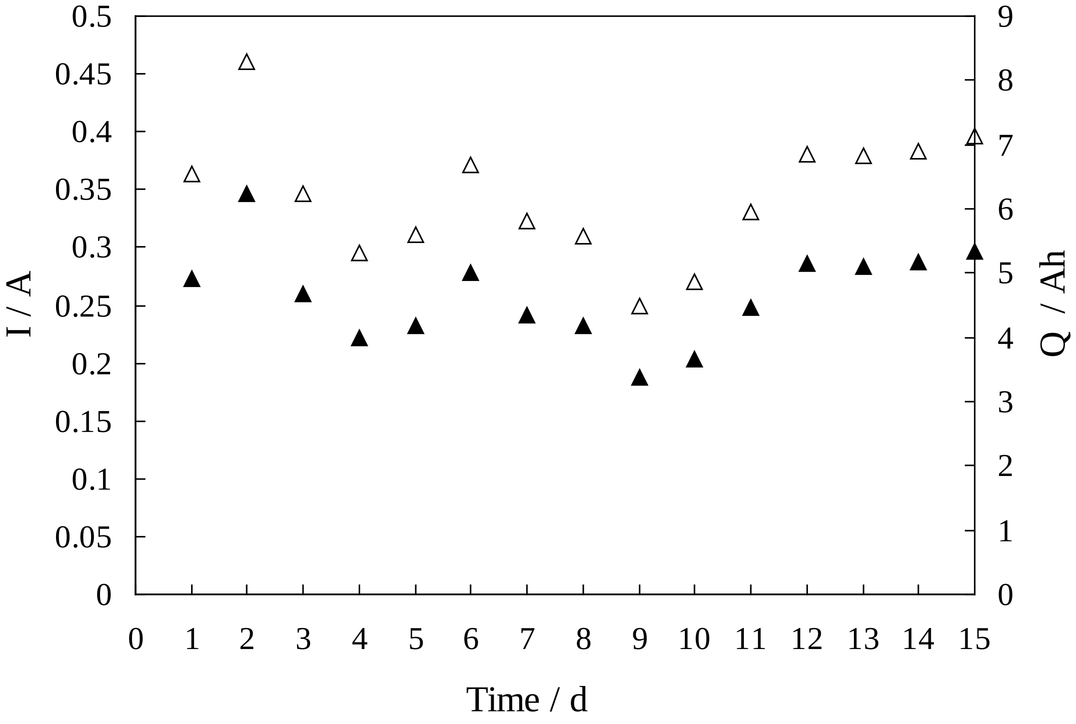
Figure 1.


600
500
400
300
200
100
0
Power irradiated / w m^{-2}
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Time / d
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
I / A
90
80
70
60
50
40
30
20
10
0
Q / Ah
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Time / d

a)

b)

Figure 1.



0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
I / A
9
8
7
6
5
4
3
2
1
0
Q / Ah
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Time / d

Figure 2

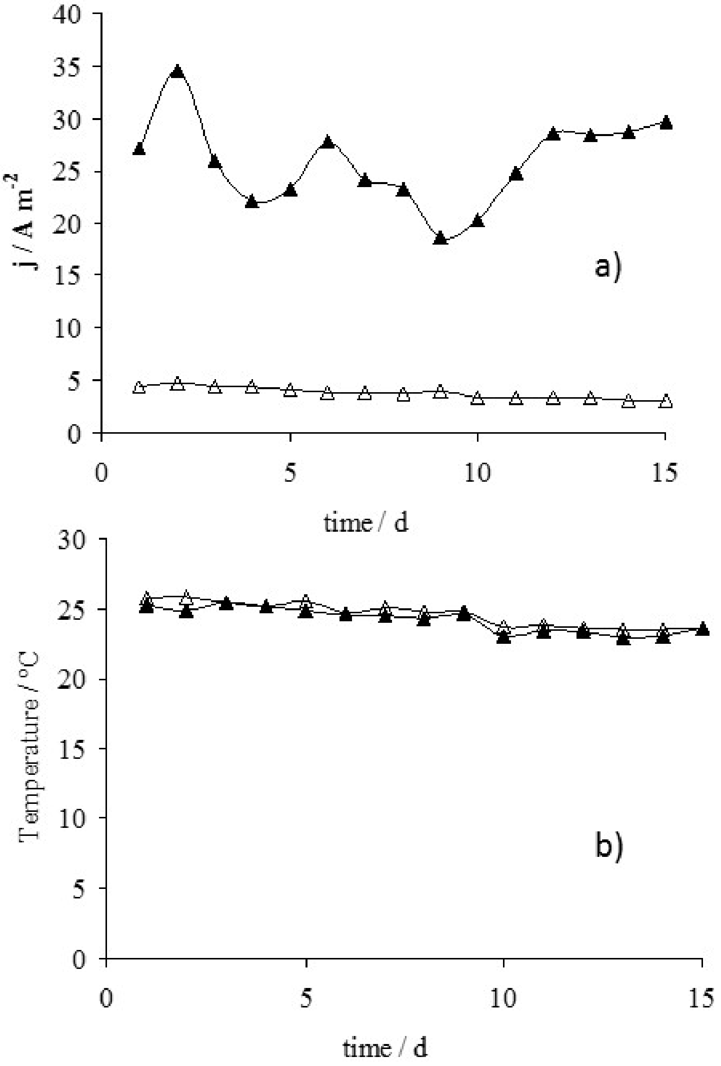

j / A m^{-2}
0
5
10
15
20
25
30
35
40
a)
time / d
0
5
10
15
Temperature / °C
0
5
10
15
20
25
30
b)
time / d
0
5
10
15

Figure 3.

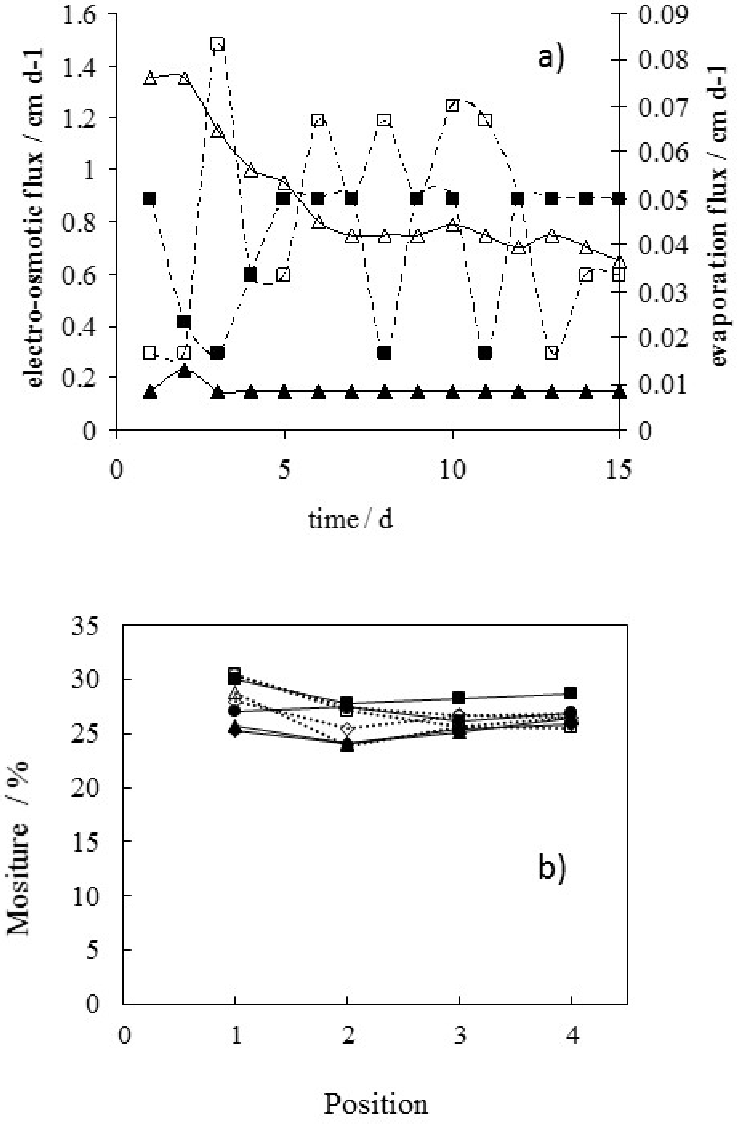

a)
electro-osmotic flux / cm d-1
evaporation flux / cm d-1
time / d
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0
5
10
15
b)
Mositure / %
Position
0
5
10
15
20
25
30
35
0
1
2
3
4

Figure 4.

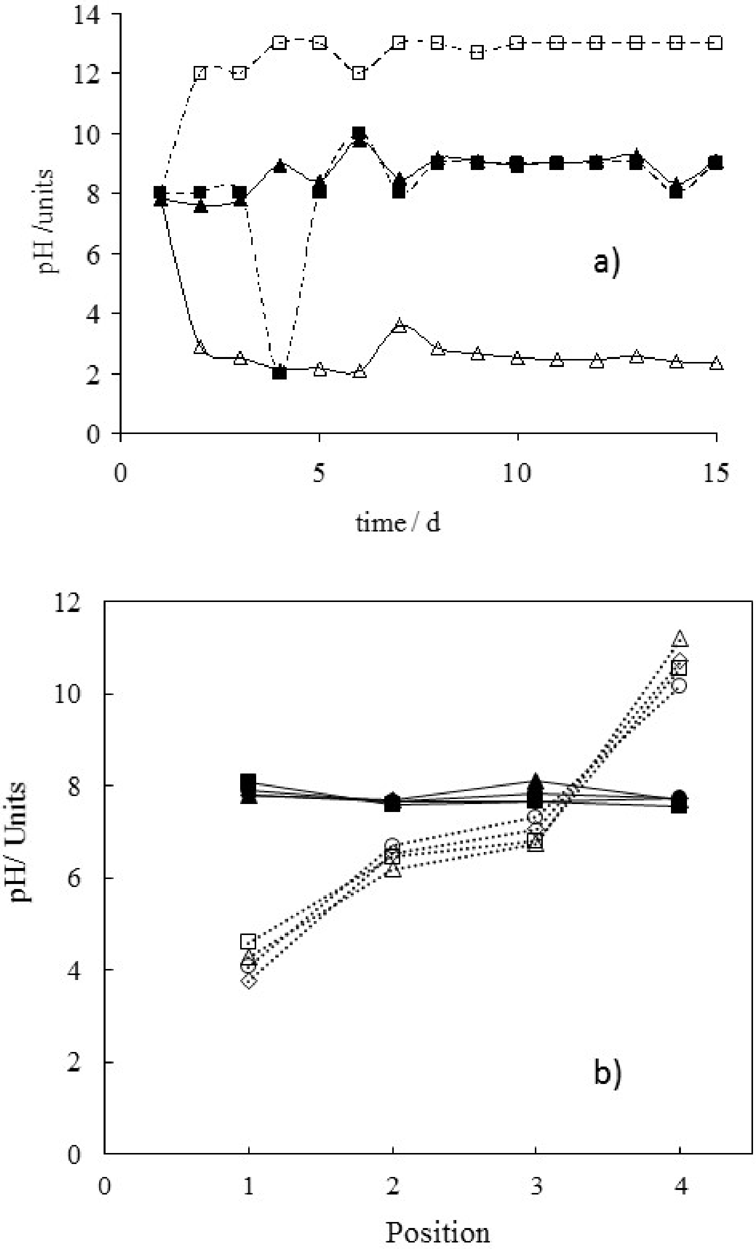

14
12
10
8
6
4
2
0
pH /units
a)
0
5
10
15
time / d
12
10
8
6
4
2
0
pH/ Units
b)
0
1
2
3
4
Position

Figure 5.

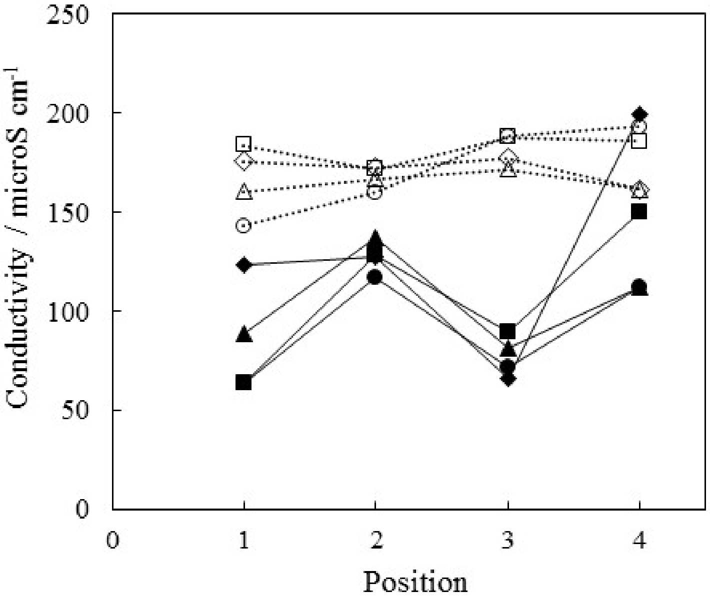


Figure 6.

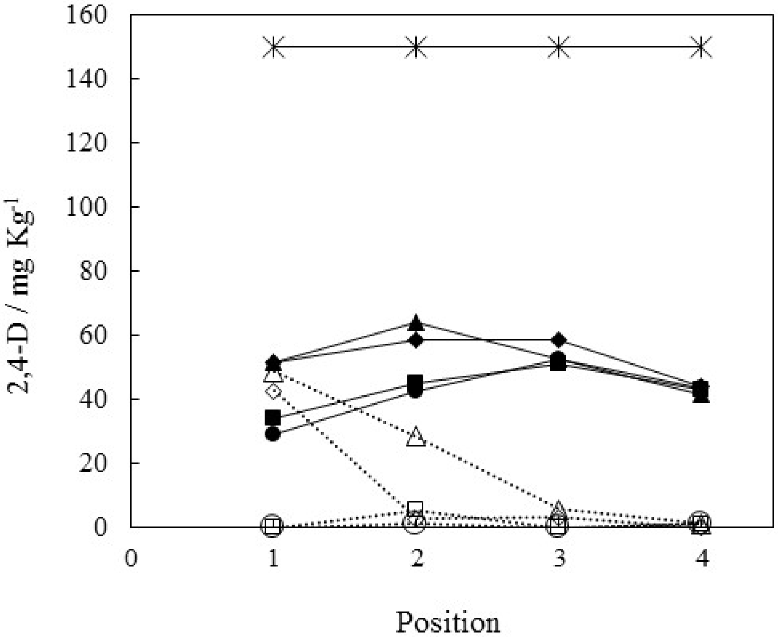


Figure 7.