Prediction and Management of Solar Energy to Power Electrochemical Processes for the Treatment of Wastewater Effluents

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Abstract

A highly versatile software tool able to predict and manage the solar power coming from photovoltaic panels and to assess the environmental remediation of wastewater effluents has been developed. The prediction software tool is made up of four modules. The first one predicts the solar radiation by a phenomenological model. Secondly, an energy optimization algorithm manages the solar power towards the third and fourth modules, an environmental remediation treatment (electrooxidation) and an energy storage system (redox flow battery), respectively. The software tool is aimed to the best solar power management to obtain the highest remediation treatment. Results shows a daily solar radiation prediction with a high accuracy, attaining correlation coefficients of 0.89. Furthermore, the prediction of the removal of an organochlorinated compound from a wastewater effluent at different time of the year was studied. Different percentages of the total solar power are sent directly to the electrooxidation reactor and to the redox flow battery. At non-solar production hour, the electrooxidation reactor is powered by the redox flow battery in order to exploit the total solar power produced. The results show that, the higher the solar radiation, the higher the power percentage that must be directly sent to the electrooxidation treatment in order to attain the best energy management and the higher remediation. Thus, an 82.5 % of the total solar power must

be sent to the electrooxidation treatment in summer days in contrast to the 17.5 % that have to be powered in winter days to attain the highest removal of pollutant.

Consequently, it is important to evaluate the connection between devices to get the best green energy management and the lower energy losses.

Keywords

Energy management; solar power; green sources; electrolysis; redox flow batteries; forecasting

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1. Introduction

Sustainability is one of the most important challenges nowadays. Humankind is facing now one of the most complex moments in history, because of the extensive and uncontrolled use of the natural resources and the important damages to the environment associated to the manufacturing processes. In order to make these changes reversible, rethinking most of the current technologies, including environmentally friendly technologies, is mandatory. The production and the massive use of a wide variety of synthetic compounds have led to a high level of pollution in soil and water effluents. Consequently, many technologies have been studied to remove different types of compounds from these natural sources. Electrochemical advanced oxidation processes (EAOPs) have shown huge removal efficiencies of organic pollutants. These technologies use the electron as almost unique reactive. Thus, the coupling of these devices with renewable energies (REs) could turn these processes into more sustainable and

environmentally friendly technologies. Taking into account the concept of integral water cycle, water effluents can be returned to their natural environments after being used and treated with a low environmental impact in a more sustainable way using renewable energies as unique reactive.

Among the huge diversity of renewable energies, the solar power has shown a huge number of advantages for being used in the powering of EAOPs. Thus, many researchers have focused their studies on the use of green energies to power electrochemical processes. The coupling of green energies and electrochemical technologies can be developed in different ways: (a) Storage and subsequent power, (b) random direct coupling, (c) targeted direct coupling and (d) targeted storage and direct coupling. Many studies have tested the behavior of electrochemical remediation technologies coupled with traditional batteries (Lead-acid batteries) [1, 2] where the renewable energy (RE) is stored and subsequently, this stored power is supplied to the remediation process. This operational mode avoids the fluctuations of the solar power production and allows working at low or null production hours. However, this involves energy losses due to the conversion efficiencies among chemical and electrical energies. Besides, it is important to note that the capacity and power of the traditional batteries is limited and could not be high enough to supply the required energy EAOPs. Conversely, the huge flexibility of energy storage in RFBs by increasing the number of electrodes (higher power) or the concentration of active species (higher capacity), make them the best alternative to storage or supply energy in a wide range of power [3].

On the other hand, the direct coupling of solar panels and electrochemical technologies has also been reported in literature [4-8]. Until now, most of the researches have shown the direct coupling EAOPs-REs using batch setups. In this case, electrochemical reactors are charged with a constant volume of wastewater and directly

73 powered by a solar panel until a complete pollutant mineralization regardless the optimum
74 operational conditions. Besides, the uncontrolled and direct powering of renewable
75 energies and electrochemical treatments have shown mass transfer problem or reversible
76 reactions when the applied current densities are excessively high or low, respectively [9].

77 The power coming from renewable energies depends on daily time, seasonal
78 variability, weather conditions and geographical location. Thus, it is not easy to forecast,
79 although it is an important challenge nowadays in which the work of many research
80 groups and companies is focused. In addition, its intermittence makes difficult the use of
81 this renewable source in a continuous and constant mode. For this reason, the prediction
82 and storage of green energy is a key issue to overcome urgently. Working on this field,
83 additional studies have been focused on the direct coupling of EAOPs-RE working on
84 continuous mode and optimum conditions (constant electric charge density, Ah dm^{-3}) [10-
85 12]. Electric charge density is the ratio between the applied current intensity and the
86 volumetric flow that is fed to the reactor in a continuous mode. Thereby, the treatment
87 can be carried out under the optimum operational conditions that allow the maximum
88 remediation, varying the treatment flow rate according to the solar power received.
89 Besides, the prediction of solar radiation would help to the regulation of the operation of
90 electrochemical technologies powered by solar energy. Despite this fact, the direct
91 coupling of EAOPs and REs can only work at solar power production hour. Moreover,
92 the power production of PV panels could be higher than the power requirement of the
93 treatment or could exceed the electric specifications of the treatment setups. Thus, a
94 surplus of power could be wasted. Consequently, renewable energy production systems
95 must be coupled with energy storage devices in order to get the best energy management
96 and use. Energy can be stored using mechanical, electromagnetic, thermal chemical or
97 electrochemical technologies [13]. Among the wide variety of technologies that have

been used for the energy storage, one of the most promising systems for the storage of renewable energy are the redox flow batteries (RFBs) [14, 15]. This electrochemical device transforms electrical energy into chemical energy changing the composition of a liquid electrolyte made up of ion species. The main advantage of these technologies is the decoupling of capacity and power [15, 16]. This allows and makes easier the coupling among renewable energies and electrochemical technologies. Thus, the management and storage of solar power could lead to sustainable and environmentally friendly treatments for the removal of hazardous compound from soils and wastewater effluents. Although there are commercial software tools to optimize the powering with renewable energy, applications related directly to electrochemical remediation treatments are not available yet.

In view of the previous arguments, the main aim of this work is the development of a software tool capable to predict and manage the solar power produced by solar panels in order to power electrically electrochemical technologies attaining the maximum environmental remediation. Thus, soils and wastewater effluents can be returned to their natural environment with a lower consumption of natural sources using a novel technology integrated by renewables energies.

2. Energy Optimization Tool

In previous studies, powering environmental electrochemical devices directly with green energies, an important drawback was found: many processes reversed when the green energy production was low or nil, making the processes less efficient from the viewpoint of energy consumption [9]. That observation advised in favor of the use of energy storage systems, for which the best features were shown by RFBs, aforementioned. The idea is not to store all energy produced and then, power from the

storage system the electrochemical devices. This system would have to face severe energy losses. Opposite, it was only aimed to store the surplus energy in order to maximize the efficiency of the treatment technologies in terms of the use of energy. The management of the energy produced with such a complex system needs for a software tool capable to forecast the solar radiation and to predict the performance of two electrochemical devices powered with changing energy profiles: a redox flow battery and an electrolytic wastewater treatment cell. Figure 1 shows a scheme of the proposed software tool. The first module predicts the solar radiation using a phenomenological model. This radiation allows to determine the generated solar power for a given solar panels system using an empirical model connected, in a second module, to a distribution energy algorithm. Then, a third and a fourth modules predict the environmental remediation of a wastewater effluent using an electrochemical treatment and the energy storage capacity of an RFB, respectively, allowing the later implementation of an energy optimization algorithm. The core of all the modules is a dedicated model. In every case, a pragmatic view was applied looking for, not only for a complete description of the processes occurring in each of the devices but for information which can be used easily in energy management.

For each module, the development of the different models that make up the software tool has followed the next steps: formulation, estimation of parameters and validation. In this work, the two first steps will be exposed with the aim of showing how to develop a robust tool that help in the design of more sustainable processes.

Figure 1. Scheme of the prediction software tool

a. Solar Radiation Prediction Module (SRPM)

The core of this Module is a model capable to predict solar radiation based on the cyclic behavior of this parameter in preceding years and on the particular weather conditions of the days preceding the forecast. A simple and pragmatic model based on time series was proposed in order to attain a robustness prediction. The proposed model takes into account two periodicities: yearly and daily.

To face the year periodicity (period 365 days), equation 1 shows the expected daily solar radiation (R) values, where t expresses time in days of the year (January 1st is day 1 and December 31st is day 365), φ_R represents the phase lag, that is the day with the maximum solar radiation received and $R^{\min}$ and $R^{\max}$ are the lowest and highest values that can take the solar radiation over the year.

$$R = R^{\max} + (R^{\max} - R^{\min}) \cdot 0.5 \cdot \left(1 + \sin\left(\frac{2\pi}{365} \cdot t + \frac{2\pi}{365} \cdot \varphi_R\right) \right) \quad [1]$$

To face the daily periodicity over the daily period of 24 hours(δ), Equation 2 is proposed, where t_{sunrise} and t_{sunset} represent the hours when the Sun rises and drops every

day, respectively, in the particular location where the model is applied and t' expresses daily time in hours (0.00 stands for 0:00 h and 23.98 for 23:59 h).

$$\delta = \text{sen}\left(\frac{\pi}{t_{\text{Sunset}} - t_{\text{Sunrise}}} \cdot (t' - t_{\text{Sunrise}})\right) \quad [2]$$

Again, t_{Sunrise} and t_{Sunset} have a year periodicity and they have to be modelled according to this fact by using equation 3 and 4, respectively, where t^{max} and t^{min} represent the maximum and minimum sunrise and sunset hours. Finally, φ_{Sunrise} and φ_{Sunset} are the phase lags that represent the days that the sunrise and sunset hours are maximum. These constants were estimated using theoretical values taking into account that the maximum sunrise and sunset hours take place the shortest (21st of December) and the longest (22nd of June) day of the year, respectively.

$$t_{\text{Sunrise}} = t_{\text{Sunrise}}^{\text{max}} + (t_{\text{Sunrise}}^{\text{max}} - t_{\text{Sunrise}}^{\text{min}}) \cdot 0.5 \cdot \left(1 + \text{sen}\left(\frac{2\pi}{365} \cdot t + \frac{2\pi}{365} \cdot \varphi_{\text{Sunrise}}\right)\right) \quad [3]$$

$$t_{\text{Sunset}} = t_{\text{Sunset}}^{\text{max}} + (t_{\text{Sunset}}^{\text{max}} - t_{\text{Sunset}}^{\text{min}}) \cdot 0.5 \cdot \left(1 + \text{sen}\left(\frac{2\pi}{365} \cdot t + \frac{2\pi}{365} \cdot \varphi_{\text{Sunset}}\right)\right) \quad [4]$$

Both periodicities are integrated into a single model by multiplying the factors proposed. Thus, equation 1 can be drawn as follow:

$$R = \text{sen}\left(\frac{\pi}{t_{\text{Sunset}} - t_{\text{Sunrise}}} \cdot (t' - t_{\text{Sunrise}})\right) \cdot \left[R^{\text{max}} + (R^{\text{max}} - R^{\text{min}}) \cdot 0.5 \cdot \left(1 + \text{sen}\left(\frac{2\pi}{365} \cdot t + \frac{2\pi}{365} \cdot \varphi_R\right)\right)\right] \quad [5]$$

In view of the previous statements, the model can only predict a theoretical behavior of the solar radiation. Nevertheless, this variable may be affected by unpredictable weather conditions. Thus, at this point, the daily solar radiation was adjusted using an additional term able to reassess the predicted solar radiation taking into account the deviation between the real and the forecasted solar radiation. This deviation has been estimated as function of the actual-predicted solar radiation ratio in a previous day. Thus, the solar radiation is multiplied by a new term, *weather factor*, which

represents the grade of deviation in terms of parts per one. Besides, with the aim of giving a realistic point of view to the weather factors, they have been related with common weather conditions regards the level of cloud cover that can reduce the solar radiation. Thus, the weather factor varies between 0 and 1, being 1 the lower deviation between actual and predicted data (sunny day). Conversely, 0 corresponds with a completely cover sky (dark hour). Table 1 shows the values and meaning of the weather factors, that represent the meteorological conditions changes that may affect the daily solar radiation. The worst the weather conditions, the lower the value of the weather constant. Thus, the theoretical solar radiation that is predicted using the base model can be reassess proportionately to the meteorological conditions of the previous day.

Table 1. Weather factors

Weather type	value
Sunny	1
Sun and clouds	0.75
Cloudy	0.5
Rainy	0.25
Dark	0

In order to evaluate the accuracy of the model, predicted vs real data were confronted with the aim of determine the relation between them in terms of correlation coefficients. This statistical parameter shows the deviation between the predicted and actual data. Thus, correlation coefficient close to 1 express a high precision of the model. Actual data from were provided by METEO Ciudad Real [17] during 2016 were used. Figure 2a shows the real and the predicted sunrise and sunset hour according to equations 3 and 4. Besides, Figure 2b shows the fitting between real and predicted sunrise and sunset hours.

As expected, the model follows a sinusoidal behavior. Regarding the maximum of each function, the maximum sunset hour can be easily differentiated at first sight on the central days of the year. Conversely, the minimum sunset hour can be seen at the end of the year. It should be highlighted that the real data show a noisier signal and two stairs around the days 90 and 300, which correspond with the variations of the standard clock time on spring and autumn that are carried out in all the European countries. Besides, Figure 2b shows that the proposed model has a high accuracy reproducing the real data, showing a better adjustment for sunset hours ($r^2 = 0.954$). In view of the previous results, it can be claimed that the formulated equations that represent the behavior of sunset and sunrise hours over the year, predict the real data with a huge level of confidence.

Figure 2. Predicted (grey) and real (black) sunrise and sunset hours (a). Predicted vs real sunrise and sunset hour (b). Real data 2016.

Once the first part of the module was evaluated, the parameters that depend on the daily solar radiation were estimated. Figure 3 shows the raw data and the modelling results for the base model and the improved model using weather constants. As expected, predicted and real data show a sinusoidal trend in both cases. Nevertheless, the base model is not able to represent the meteorological condition changes that can affect the received solar radiation. Conversely, Figure 3b shows the predicted maximum solar

radiation peaks closer to the real ones, reproducing with a higher precision the real solar radiation. In order to corroborate the results attained, predicted versus real solar radiation data were fitted and correlation coefficients were calculated. The correlation coefficients took values of 0.727 and 0.795 for the base and the improved prediction models, respectively. As expected, the use of weather constants increases the accuracy of the model, being close to the real data. Doorga et al. [18] reported correlation coefficients lower than 0.72 in most of the forecasting models studies, attaining a lower accuracy in the prediction of solar radiation. In order to have these accurate predictions, all the fitting parameters are shown in Table 2.

Table 2. Values of the fitted parameters

Parameter	Value
$R^{\max}$ (W m ⁻²)	1500
$R^{\min}$ (W m ⁻²)	500
ϕ_R (day)	-65
$t_{Sunrise}^{\max}$ (h)	8.8
$t_{Sunrise}^{\min}$ (h)	7.0
$\phi_{Sunrise}$ (day)	-80.75
$t_{Sunset}^{\max}$ (h)	21.8
$t_{Sunset}^{\min}$ (h)	18.0
ϕ_{Sunset} (day)	-264.75

Figure 3. Real (■) and predicted (■) solar radiation. (a) Base model and (b) model modified adding weather factors. Real data: 2016.

With the aim of knowing in depth the precision of the model, correlation coefficients and Root Mean Square Errors (RMSEs) were calculated for each month of the year. Figure 4 shows the RMSEs and the correlation coefficients for each month of the year for the base and improved models. Results show higher errors for the central months of the year in both cases. The fittings took the highest correlation coefficients on September regardless the level of precision of the model ($r^2 = 0.894$). Conversely, the lowest correlation coefficients were attained on March and May, being over 0.66 for all

the months in the improved model. The lowest correlation coefficients attained in spring months could be related to the high variability of weather conditions in these months of the year. Other authors reported monthly and seasonal RMSEs showing the same trend that has been exposed previously, huge error in spring months [19, 20]. On the contrary and despite the low probability of rainy and cloudy days in summer, higher errors and consequently lower correlation coefficients were attained in June and July months, even after the model was improved using the weather factors. The lower the forecasting horizon, the lower the RMSEs. Thus, in order to increase the accuracy of the model, the forecasting horizon must be reduced. Nevertheless, the results have shown RMSE values in the same order of magnitude than others reported by Beniali et al. [20] using other forecasting models.

Figure 4. RMSEs and correlation coefficients. Base model (■) and model modified adding weather factors (■). Real data: 2016.

a. Energy Management Module (EMM)

The second part of the model is related to the energy management. Once the solar radiation is known, it is important to estimate the amount of energy (Wh) that a particular set of solar panels can generate with regard to the solar radiation that arrive to them. After that, the total power can be managed in order to send the optimum one to each electrochemical device. Experimental data from two photovoltaic (PV) panels connected in parallel from ATERSA (Spain) (area of 1.313 m² each panel) and located on the roof of the labs (38.59 N 3.55 O) were used to determine a curve that relates the received solar radiation and the electric solar power. Table 3 shows the main specification of the solar panels. Previous studies of our group determined a relation between the solar radiation and the electric power generated in the PV panels [6]. Figure 5 shows the experimental curve that represents the energy management module. The data were fitted using a second order equation attaining a correlation coefficient of 0.98 (equation 6). Besides, this model is in charge of managing the electrical solar power to supply electrically the environmental treatment and the energy storage system. Different percentages of power can be sent to each electrochemical device to obtain the higher environmental remediation.

Table 3. PV panel specifications

Model	A - 160M
Power (W)	160 W
Isc (A)	5 A
Voc (V)	43.90 V
Fill Factor (%)	73
Solar declination (°)	45
Panel area (m²)	1.313

$$\text{Electric Power (W)} = 0.0006 \cdot \text{Solar Radiation}^2 + 0.078 \cdot \text{Solar Radiation} \quad [6]$$

Figure 5. Electric solar power vs Solar radiation.

b. Environmental Remediation Treatment (ERT) and Energy Storage (ES) Modules

Simplicity is, perhaps, the most important feature of a robust model. In modelling of electrochemical processes, there are many different approaches from those based on very simply assumptions and globalized parameters to others based on the lumped description of many different species using CFD (Computational Fluid Dynamic), passing through many intermediate-complexity models. The choice depends on the application and should be carried out based on pragmatism. In the system developed in this work, models based on electrochemical devices must reproduce how energy can be stored or how pollution is degraded with a time-changing pattern depending on the applied power. Then, there are two major aspects that must be covered: 1) how to transform power supplied/consumed by an external device into current intensity and cell voltage and 2) how relevant species concentration changes inside the electrochemical reaction system.

To face the first point, it must be taken into account that cell voltage in an electrochemical cell is composed by several terms as shown in equation 7. Some of them depend on the current intensity; others not. In addition, power obtained/consumed in an electrochemical cell can be calculated by the multiplication of the cell voltage and the current intensity as equation 8 shows. This means that for a given applied power, depending on the operation mode, there is only one feasible pair V-I.

$$E = E^0 + \eta_A + \eta_C + \sum I \cdot R \quad [7]$$

$$P = E \cdot I \quad [8]$$

As equation 7 shows, the cell voltage is made up of different components such as reversible cell voltage (E^0), overvoltages (η_A and η_C are the anodic and cathodic overvoltage, respectively) and drops [21, 22]. If the process is controlled by the transfer of electrons or ions to the electrode or electrolyte interface, then a relationship between current density (j) and voltage can be drawn as follow:

$$j = j_0 \cdot \left[\frac{C_O(0,t)}{C_O^*} \cdot e^{-\alpha \cdot \frac{F}{R \cdot T} \eta} - \frac{C_R(0,t)}{C_R^*} \cdot e^{(1-\alpha) \cdot \frac{F}{R \cdot T} \eta} \right] \quad [9]$$

Where, $\eta = E - E^0$, j_0 is the exchange current density, α is the transfer coefficient, R is the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvin and F is the Faraday constant ($96485.33 \text{ C mol}^{-1}$). Besides, C_i and C_i^* , represent the concentration of oxidant (C_O) and reductant (C_R) in the electrode surface and the bulk solution, respectively.

On the other hand, when the process is not affected by the mass transference, the concentration on the surface electrode and into the bulk solution can be considered the same. Thus, equation 9 turns into equation 10, known as *Butler-Volmer* equation [23]. Besides, when the process is no limited by the transport of reactant species to the electrodes, Butler-Volmer equation turns into Tafel equation (equation 11), which shows

an exponential behaviour of the voltage with the current intensity for overvoltage over 100 mV [23, 24].

$$j = j_0 \cdot \left[e^{-\alpha \cdot \frac{F}{R \cdot T} \eta} - e^{(1-\alpha) \cdot \frac{F}{R \cdot T} \eta} \right] \quad [10]$$

$$\eta = a + b \cdot \ln [I] \quad [11]$$

Otherwise, the cell potential could be correlated to the surface concentration of the oxidant and reductant species by Nernst equation, equation 12.

$$E = E^0 + \frac{R \cdot T}{F} \cdot \ln \left[\frac{C_O(0,t)}{C_R(0,t)} \right] \quad [12]$$

Consequently, in view of the previous arguments and with the aim of simplifying the model, equation 13 has been selected to reproduce the relation between voltage (V) and current intensity (I) for any electrochemical device.

$$\eta = a + b \cdot \ln(I) + c \cdot I \quad [13]$$

Regarding the environmental remediation treatment, a commercial conductive diamond electrochemical oxidation (CDEO) reactor, DiaCell[®] 101 Adamant using BDD-Nb electrodes (WaterDiam) was selected as a model of electrorremediation reactor (78.5 cm²) which was operated in continuous mode. Otherwise, a vanadium redox flow battery (40 cm²) provided by Baltic Fuel Cell was selected as electrochemical energy storage device. A commercial vanadium solution provided by OXKEM (1.6 M V³⁺, 2M H₂SO₄ and 0.05M H₃PO₄) was used as electrolyte in both compartments. Besides, carbon soft felt (SGL Carbon) and Nafion[®] 117 were used as electrodes and protonic membrane, respectively.

As aforementioned, the cell potential depends on different resistances. It should be pointed out that one of the resistance terms is related to the electrolyte conductivity. The

higher the conductivity, the lower the cell resistance. Consequently, higher resistances lead to a higher cell voltage. Thus, relation between voltage and current was estimated for both electrochemical devices. Firstly, V-I curve for the electrolysis reactor was determined using equation 13. As explained before, the resistance of the cell depends on the electrolyte conductivity. Thus, the parameters that make up the voltage function were estimated using different effluents, tap water and a soil washing effluent with conductivities around 439 and 1120 $\mu\text{S cm}^{-1}$, respectively. Table 2 shows the values of the constants that fit equation 13 for both effluents. Only slight differences can be observed for the terms a and b. Nevertheless, the term c, which has more influence into the cell voltage, shows a value over three times greater for the tap water. As expected, these values expose the higher resistance offered by the tap water which presents a lower conductivity.

Table 4. Constants of V-I curves

Effluent	a	b	c
Tap water	4.77	0.31	1.94
Soil washing effluent	4.80	0.39	0.61

On the other hand, the voltage equation for the RFB was determined considering the variations of vanadium species concentration by Nernst equation. Thus, equation 13 can be drawn as follow, where V_{RFB} ...

$$V_{\text{RFB}} = 1.26 + \frac{8.314 \cdot T}{F \cdot n} \cdot \ln \left(\frac{[\text{V}^{+5}] \cdot [\text{V}^{+2}]}{[\text{V}^{+4}] \cdot [\text{V}^{+3}]} \right) + 0.005 \cdot \ln(I_{\text{RFB}}) + 0.0064 \cdot I_{\text{RFB}} \quad [14]$$

To face the second point, from a simplistic point of view, the electrochemical cells and the possible reservoir tanks in which most of the electrolytes are contained can be

understood as a single stirred tank reactor, equation 15. In addition, the reaction term can be easily related to the applied current intensity by equation 16 in which the efficiency in the production of the desired product is set by the parameter η . This globalized-parameter approach is more than enough to reproduce accurately the behavior of electrochemical systems. The application of these types of modelling to the electrochemical devices has some particularities. Some terms of the equation 15 should be removed depending on the operation mode and the species involved in the reaction. In continuous mode, a constant flow goes in and out of the cell varying the species concentration according to the current density applied. Conversely, in batch mode, a constant volume is charged to the reactor and there are not inlet and outlet streams. Furthermore, it is important to note the behavior of divided cells. In this case, the mass balance must be carried out for each compartment of the cell. In addition, the generation terms will take positive or negative values if there is a generation or degradation process, respectively. It must be highlighted that the reactions that take place in a redox flow battery are reversible. In this case, the mass balance will be expressed in the discharge step.

$$[Acumulation] = [Inlet] - [Outlet] + [Generation] \quad [15]$$

$$\frac{V \cdot dC_t}{dt} = q \cdot C_0 - q \cdot C_t + r \cdot V = q \cdot (C_0 - C_t) + \frac{I \cdot V}{n \cdot F} \cdot Eff \quad [16]$$

The degradation of an organochlorinated compound (cloparylid) was selected as hazardous model compound to study the behavior of an electrooxidation treatment working under continuous mode, equation 17.

$$[Clop]_t = [Clop]_{t-1} + (t - t_0) \cdot \left[\frac{q_v}{V} \cdot ([Clop]_{t_0} - [Clop]_{t-1}) - \frac{I}{n \cdot F} \cdot Eff_{EAO} \right] \quad [17]$$

Where, t expresses time in hours, v (L) is the reaction volume, q_v (L s⁻¹) is the volumetric flow, n is the number of electrons exchanged in the electrochemical process, F is the Faraday constant (96485 C mol⁻¹).

On the other hand, equation 16 can be drawn as follow to represent the behaviour of active species into the redox flow battery taking into account the previous statement. Thus, equations 18 and 19 show the concentration of vanadium species in the positive and negative electrolyte compartments, respectively, according to the discharge step. Once known the concentration of one of the species and taking into account the bulk concentration of vanadium, the concentration of the other vanadium species could be known.

$$[V^{+5}]_t = [V^{+5}]_{t-1} + A \cdot \frac{(t-t_0)}{V_{\text{Electrolyte (+)}}} \cdot \frac{I_{\text{RFB}}}{n \cdot F} \cdot Eff_{\text{RFB (+)}} \quad [18]$$

$$[V^{+3}]_t = [V^{+3}]_{t-1} + A \cdot \frac{(t-t_0)}{V_{\text{Electrolyte (-)}}} \cdot \frac{I_{\text{RFB}}}{n \cdot F} \cdot Eff_{\text{RFB (-)}} \quad [19]$$

Where $[V^{+n}]$ represents the concentration of each vanadium specie and $[V]$ is the total vanadium concentration (1.6 M). As explained before, the previous equations express the variation of the vanadium species in the discharge step. In order to differ the charge and discharge processes, a constant has been added and labelled as A . This constant, A , will take the value of 1 or -1 if the RFB is charging or discharging, respectively.

As it was exposed previously, the purpose of this software tool is the management of green energy to aim at new environmental remediation treatments. Thus, with the aim of evaluating the proposed models, the degradation of an organochlorinated compound (clopyralid) was experimentally studied using solar power. The concentration of pesticide

was measured by high performance liquid chromatography, HPLC (Agilent 1260 Infinity), as reported elsewhere [11].

In contrast to the traditional operation mode of electrochemical technologies (galvanostatic mode), variable current densities coming from solar panels were applied to an electrolysis process. Figure 6a shows the solar radiation profile used to power the electrooxidation reactor during 15 days of treatment. Figure 6b shows the experimental and the predicted concentration of clopyralid removed when variable current densities were applied to the electrooxidation reactor. In both cases, the results do not show organic removal when solar radiation does not face to the PV panel and consequently, current density is not applied to the electrooxidation reactor. However, the higher the applied current density, the higher the attained remediation. Typically, the electrochemical oxidation of diluted wastes leads to the almost direct mineralization of the pollutants with extremely low concentrations of intermediates as reported elsewhere [1]. In this case, this almost negligible values were confirmed by HPLC.

Regarding the precision of the model, the predicted data expose a similar behavior than the experimental one, achieving a correlation coefficient around 0.70. These results confirm the huge accuracy of the model to predict the degradation of an organochlorinated compound using solar energy to power the electrochemical treatment.

Figure 6. (a) Solar radiation profile in Ciudad Real (Spain) during fifteen days (23rd January to 9th February). **(b)** Predicted (—) and experimental (●) concentration of clopyralid during fifteen days of electrooxidation treatment. $[\text{Clopyralid}]_0 = 400 \text{ ppm}$, $q_v = 2 \text{ L day}^{-1}$.

3. Case of study

As aforementioned, the target of the present work is to predict the environmental remediation of wastewater effluents using green energies as unique reagent. Consequently, the prediction of the removal of an organochlorinated compound using an electrolysis reactor powered by solar energy was studied. The study was developed at four different months of the year, corresponding with the different annual seasons. In order to determine the operational conditions of the electrochemical devices (EAOP and RFB), a conservative approach regard daily solar power production was determined, 2200 Wh. Thus, considering the V-I curves of each electrochemical system the volumetric treatment flow was set at 53.5 L day^{-1} . Conversely, each compartment must contain 61.2 L of electrolyte to attain a capacity of 2623 Ah.

Figure 7 shows the real and predicted solar radiation (using the model proposed) for the first fifteen days of each month. As expected, the higher and lower solar radiation values were attained in summer and winter, respectively. Besides, it can be observed a

slightly increase of solar radiation as the days go by in spring days. Conversely, the opposite behaviour can be seen in autumn days. In order to know the accuracy of the predicted solar radiation pattern, correlation coefficients were calculated for each month. Those fitting parameters took values from 0.73 to 0.92, which correspond with the months of March and September, respectively. These data corroborate the results exposed previously which show a lower accuracy for spring months.

Once known the solar radiations for each month and consequently, the power generated by the PV panels, different percentages of the total solar power were supplied to the environmental remediation process, storing the surplus in the modelled RFB. Thus, the degradation of 400 ppm of clopyralid was studied during 15 days of treatment with the aim of knowing the best energy management to attain the highest environmental remediation. Figure 8 shows the total clopyralid removed according to the solar power percentage supplied to the electrooxidation process in the different months studied. As expected, the higher the solar radiation, the higher the removal of clopyralid. Nevertheless, as previous studies show, the higher the current density, the lower the removal efficiency of the process [25-28]. Consequently, working at the optimum constant electric charge density allow to attain the higher removal efficiencies. Thus, it is important to determine the total power that must be sent to the electrochemical remediation treatment in order to avoid the waste of energy in secondary reactions that reduce the removal efficiency of the process.

Besides, the results shown that when all the solar power is supplied to the electro-oxidation process, a lower remediation is achieved. Consequently, a percentage of the solar power must be stored in order to exploit all the power generated by the PV panels. Otherwise, results expose that the amount of energy that must be supplied to each electrochemical device in order to attain the maximum environmental remediation, varies

according to the time of the year. As Figure 8 shows, the higher removal of clopyralid in summer days would be attained when almost an 82.5 % of the solar power is provided directly to the electrochemical treatment, storing the surplus. In contrast, a 17.5 % of the total power must be provided to the remediation process in winter days in order to rise the higher removal of clopyralid. It is important to note that the higher is the power sent to the energy storage device, the lower is the total energy used due to the possible loss related to the storage process.

Figure 7. Real (---) and predicted (—) solar radiation for the first fifteen days of March (a), June (b), September (c) and December (d). Real data: 2016.

Figure 8. Total clopyralid removed vs power percentage sent to the electrooxidation process during the 15 days of treatment each month. (■) December, (●) September, (x) March and (▲) June. $[\text{Clopyralid}]_0 = 400 \text{ ppm}$, $q_v = 53.6 \text{ L day}^{-1}$.

4. Conclusions

From this work, the following conclusions can be drawn:

- A highly versatile software tool was developed in order to predict and manage the removal of hazardous compounds from a polluted effluent by electrolysis.
- Solar radiation can be forecasted using a simple model with a good reproducibility and robustness. Likewise, the removal of organochlorinated compounds using an electrooxidation reactor powered by solar panels has been predicted with a high level of precision using a pragmatic model which accounts only for the more relevant processes happening in the cell.
- The amount of energy that must be delivered to the remediation treatment or to the storage system depends on the season of the year. Thus, in summertime is recommended to supply more energy directly to the electrochemical reactor and in winter to the battery in order to optimize the removal of pollutant.

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