Towards the sustainable powering of the electrocoagulation of wastewater through the use of Solar-Vanadium Redox Flow Battery: a first approach

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ABSTRACT

Electrocoagulation (EC) of wastewater polluted with 100 mg dm⁻³ of oxyfluorfen (OFF) has been studied in cells with iron anodes and aluminum cathodes. Solar power combined with energy storage in a vanadium redox flow battery (VRFB) has been used to electrically power a continuous EC process. Three scenarios have been evaluated. Firstly, a constant current was applied to the EC reactor. Secondly, a solar energy profile was applied to the EC reactor and the RFB. Finally, the EC process was operated in the same way as the second scenario except that the RFB was powered with double the current charge than in the second scenario. The results show that electrocoagulation is not suitable for the complete removal of oxyfluorfen from wastewater, although it attained a significant pollutant accumulation into the flocs of 25%, showing potential as a pretreatment for this kind of waste. Likewise, results obtained pointed out that electrocoagulation can be powered directly with solar energy and this energy can also be regulated by VRFB, although, in the latter case, to attain the same treatment efficiency, around 1/3 more energy is required during energy storage. In addition, the higher the energy provided by the VRFB is, the lower the Fe/Al ratio produced during the electrocoagulation is.

KEYWORDS

Redox flow battery, electrocoagulation, solar energy storage, pesticide

1. INTRODUCTION

In recent years, the use of pesticides to improve agricultural productivity has increased considerably. This improvement has made it possible to cultivate a wider variety of vegetables used for human or animal consumption. However, the overuse of these substances has some disadvantages, such as the loss of fertile farmland, ground acidification, nitrate lixiviation and loss of biodiversity [1]. Consequently, it is necessary to remove them from the polluted groundwater or farmlands. Most of the pesticides used have great chemical stability, resistance to biodegradation and high water insolubility. These are therefore the most problematic characteristics for the environment and, consequently, for human health.

The degradation of oxyfluorfen in water and soils has been previously reported. Photolysis of oxyfluorfen in organic solvents [2] and electrolysis of wastewater using DDB (Diamond Doped Bore) as an anode [3, 4] have achieved higher degradation efficiencies. In order to efficiently remove these pollutants from liquid waste, a recent work by our group [3] proposed the use of electrocoagulation to concentrate the pollutant and later treat the concentrated waste by electrolysis. Successful results with oxyfluorfen make this technology very promising and further studies are being carried out with other emulsified species. The new technology does not aim to completely remove emulsified pollutants, but rather to concentrate them into the flocs. For this reason, oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene, OFF) was considered a good candidate because it has a low water solubility (0.116 mg dm⁻³ at 20°C), low vapor pressure (0.026 mPa at 25°C) and high organic carbon adsorption coefficient ($K_{OC} \approx 3.46\text{--}4.13$) [5]. As is well-known, electrocoagulation is based on the application of low currents, which are high enough for the oxidation of significant amounts of a sacrificial electrode (Fe and/or Al). In the case of oxyfluorfen, ions generated group around the pesticide colloids, neutralizing their superficial electric charge and forming larger particles, which are removed from the treated water by flotation, filtration or sedimentation procedures [6, 7]. Alternatively, and/or simultaneously, depending on the operating conditions, the colloids can be enmeshed into the growing coagulant precipitate and separated by the same methods. The efficiency of this treatment has been previously demonstrated for the treatment of polluted wastewater with different pesticides such as Diazinon [8] and Malathion [9].

Electrochemical treatments depend on the availability of an electricity grid. This may be a problem if the location for the treatment facility has to be in an isolated area, where the supply of electricity is limited or unavailable. In this paper, the use of renewable energy sources as a solution to this problem is proposed. Photovoltaic plants or wind turbines can be built in places where the common supply of electricity is difficult or expensive. This means that an EC plant could be built where the polluted water is present, irrespective of whether there is an electrical grid infrastructure or not. Moreover, the main drawback for the real scale application of the electrochemical treatments is usually related to the high economic cost derived from the consumption of electricity. By using renewable energy sources, this cost is null, making the wastewater treatment absolutely energy sustainable. However, renewable energy also has drawbacks, with the primary one being its absolute dependence on environmental conditions; a wind turbine will not produce electricity if there is no wind and a solar plant will not produce electricity if it is cloudy or at night [10, 11]. This means that interruptions could occur during the operation of the plant, causing a decrease in the efficiency of the treatment. The solution for this problem is the use of systems for the storage of any excess electricity that is produced, for use when necessary. Some of the most relevant storage systems are compressed air, pumped hydro, superconducting magnetic energy, flywheels or electrochemical systems (static batteries, fuel cells or redox flow cells) [12, 13]. Focusing on the latter, desirable features for the proper functioning of batteries are high charge/discharge efficiency and good performance for use during a high number of charge/discharge cycles [14]. Some of the most promising technologies that accomplish these results are redox flow batteries and, specifically, Vanadium Redox Flow Batteries (VRFBs). They have a high efficiency, a high life-cycle and a minimum auto-discharge, characteristics that have led to several companies commercializing this technology [15]. Equations 1-3 detail the reactions involved in the performance of a VRFB.

Taking into consideration this background, the main goal of this work is to evaluate the performance of electrocoagulation for the treatment of OFF polluted wastewater in continuous mode during 4 day tests, in which the electrocoagulation is powered in three different ways. During sunlight hours, the EC treatment was connected to the power supply and the electricity was provided according to the profiles required in each scenario described in Section 2. At the same time, the VRFB was charged using the same solar radiation profile. During the night hours, the energy stored in the VRFB during the day was used to supply the energy required by the EC system.

The aim is to evaluate, in a preliminary way, whether the storage of energy provided by solar panels in VRFB is suitable for this technology and to shed light on the advantages and drawbacks of this procedure.

2. EXPERIMENTAL

2.1. Methods

Figure 1 shows a scheme of the experimental setup used in this work.

Figure 1. a) EC setup, b) power supply, c) VRFB and multimeter. a+b: Daytime hours operation mode; a+c: Night hours operation mode.

The Electrocoagulation (EC) treatment of a solution containing 100 mg dm^{-3} OFF and 10 g dm^{-3} Na_2SO_4 as a supporting electrolyte was evaluated. EC experiments were carried out using a 4 dm^3 -continuous stirred tank reactor. Two 25 dm^3 -tanks were used as reservoirs for the polluted and treated water, respectively. A peristaltic pump (Reglo Digital MS-2/8, Ismatec) was used to circulate the wastewater through the reactor in a continuous operation mode. Aluminum and iron plates ($11 \times 11 \text{ cm}^2$), were used as the cathode and anode, respectively, and were directly immersed in the polluted water to be treated inside the reactor. Electrodes were connected to a power supply (ES 150-Series, Delta Elektronika) or to a VRFB (described below), depending on the operation mode. The different scenarios are described as follow:

- Scenario a: the electrocoagulation cell is powered at galvanostatic conditions during days and nights by providing a constant electric current
- Scenario b: half of the energy produced by solar panels over the sunlight period is used to charge VRFB and the other half to power the electrocoagulation cell. Overnight, the VRFB is connected to the EC until its complete discharge.
- Scenario c: same as scenario b) but powering the charge period of the VRFB with double energy power.

It is important to note that the solar profile supplied to the EC reactor and the VRFB was adjusted to avoid damage to the material of both electrochemical devices. The bipolar plates of the VRFB can be damaged at high voltages. Consequently, the solar profiles were supplied to the RFB using a Potentiostat PGSTAT 302N to control that variable in the charge cycles. Moreover, a multimeter (2000 6-1/2-Digit DMM, Keithley) was used to monitor the value of electricity supplied to the EC by the VRFB. The duration of tests was 96 h and readings were taken every 1.5 hours during the daytime.

2.1.1. VRFB

The Vanadium Redox Flow Battery (VRFB) used in this work has been supplied by Baltic Fuel Cells and is composed of two differentiated modules: a quick connect fixture (qCf-RFB) that allows the compression of the internal components of the commercial 40 cm^2 RFB cell (cF40-RFB) using a centric clamping vice. Also, qCf-RFB provides temperature regulation by pumping a thermal fluid (Huber P20.275.50) located

in an external thermostatic bath (Huber). A commercial vanadium electrolyte, supplied by Golden Energy Fuel Cell Co. Ltd. (China), was used in this work; it had a 2 M V concentration (VO^{2+} in the positive electrolyte and V^{3+} in the negative electrolyte) in 3 M H_2SO_4 . The battery was considered completely charged when the OCV reached 1.57-1.59V, as reported elsewhere [10, 11, 16]. A peristaltic pump (Heidolph Pumpdrive 5001) was used to deliver electrolyte to the RFB cell at a constant flow rate ($20 \text{ cm}^3 \text{ min}^{-1}$). Carbon soft felt, provided by SGL Group, was used as an electrodic material in both the cathode and anode. A cationic exchange membrane (STERION L-105) was used to separate the anodic and cathodic compartments inside the cell [10, 11].

2.2. Analytical techniques

Samples were taken from inlet and outlet stream reactor. Concentrations of iron and aluminum, used as coagulation agents, were quantified using an ICP-AES Liberty Sequential (Varian). The organics concentration was quantified using a Multi N/C 3100 TOC analyzer (Analytik Jena). All samples were filtered with $0.22 \mu\text{m}$ nylon filters (Scharlab) to carry out the DOC (Dissolved Organic Carbon or soluble TOC) measurements. The measurements were obtained from the sample combustion at 800°C to reach CO_2 that was measured by an infrared light laser. This parameter provides information not only on the concentration of OFF, but also about other potential intermediates that can be formed in the system throughout the treatment, giving an overall view of the soluble pollutants remaining in the wastewater. The pH and conductivity were measured using a pH meter GLP 22 and a Conductimeter GL31 (Grison instruments S.A, Barcelona, Spain), respectively.

3. RESULTS AND DISCUSSION

As stated before, high electricity consumption is one of the main drawbacks for the full scale application of electrochemical processes. For this reason, the use of green energies can be considered a booster for the application of this technology and improving the available knowledge about ways in which to maximize its efficiency is a paramount challenge, taking into account the special characteristics of this energy supply. Here, we aimed to combine photovoltaic energy with VRFB, in order to see whether a proper management of the energy obtained by the photovoltaic panels could be attained by using a VRFB to regulate the energy dosed to the electrocoagulation reactor.

In order to compare several scenarios regarding the way to manage PV energy, the solar irradiation received during four consecutive days (16th to 19th January of 2016) in winter in Ciudad Real, Spain (38.59 N 3.55 O) was monitored and used as a pattern of study (Figure 2).

Figure 2. Solar radiation profile in Ciudad Real (Spain) during four days (16th to 19th January).

As observed, the profile selected corresponds to typical sunny winter days in the south of Spain, with more of half of the day without solar light, which is the worst case scenario in a sunny country like Spain. Maximum solar radiation values were obtained around noon, and varied from day to day, ranging from 585 W m⁻² on a slightly foggy day (3rd day) to 758 W m⁻² on the sunniest day (1st day). This radiation profile was used to generate the three scenarios evaluated in this work, simulated by the potentiostat described in the experimental section. One corresponds to a plateau supply of energy to the EC with a constant current intensity, assuming a perfect and ideal regulation of the energy produced by the PV panels, which provides exactly the same value of current during all hours of the day. The other two scenarios correspond to the use of the PV energy in a more complex way: part of the energy produced is used to power the

electrocoagulation directly and another part is use to charge the VRFB. The difference between the two scenarios is that in the first one, the same amount of energy is provided to the electrocoagulation cell and to the VRFB. In the second, the energy supplied to the VRFB is doubled (so the total energy is higher by 1/3), in order to obtain a greater regulation capacity with the VRFB. In the latter two scenarios, the VRFB is used to power the electrocoagulation cell during the night. The profiles of the energy supplied to the VRFB are shown in Figure 3, while the profiles of energy supplied to the electrochemical cell are shown in Figure 4.

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218 Figure 3. Profiles of intensity powered to the VRFB in the three scenarios. a) No use of
 219 the VRFB; b) powering the VRFB with half of the intensity produced in the solar panels;
 220 and c) powering the VRFB with 2/3 of the energy provided by the solar panels.

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Figure 4. Intensity applied to the electrochemical cell. a) Constant current density; b) same amount of energy dosed to the electrocoagulation cell and to the VRFB; and c) double energy supplied to the VRFB.

The most important observation is the current discharge profile of the VRFB connected to the EC process during the night hours. As can be seen, discharge of the VRFB occurs at an almost constant value of current that, apparently, does not depend on the state of charge of the battery. However, the electricity stored in the VRFB was not sufficient to ensure the continuous electrical supply of the EC for the entire night. As observed, the higher amount of energy stored in the latter scenario enabled an almost constant supply overnight, while in the scenario where the VRFB was charged with only half of the energy

produced, no energy was powered to the electrocoagulation cell during a large part of the night. In this way, it is important to take into account that the energy storage capacity depends on the size of the electrolyte tank and the power rating depends on the vanadium concentration of the electrolyte solution [17, 18]. Consequently, these two characteristics of the VRFB can be optimized independently, according to the requirements of the electrochemical process to be electrically supplied. Figure 5 shows the charge and discharge capacities and the coulombic efficiencies of the RFB when it was charged using profiles b) and c) (shown in Figure 3) and then, directly discharged to the EC reactor overnight. The theoretical capacity calculated from Faraday's law is 10.7 Ah. However, as observed, the experimental capacities were far from this value. Higher charge capacities were obtained when the RFB was powered with 2/3 of the energy provided by the solar panels. Consequently, higher discharge capacities were obtained, allowing the EC reactor to be electrically fed for a longer time during the night. Although slight variability can be seen, the EC values in both systems are similar (in the range 60-70%) and are also comparable with those obtained in previous works, where the RFB was also charged using solar and wind power [10, 11].

Figure 5. Charge capacities (dark grey bars), discharge capacities (light grey bars) and coulombic efficiencies (■). a) Powering the VRFB with half of the intensity produced in the solar panels. b) Powering the VRFB with 2/3 of the energy provided by the solar panels.

Figure 6 shows the production of coagulant reagents during the three scenarios studied. In the EC setup, an iron sacrificial anode and aluminum cathode are used. The Fe anode undergoes electro-oxidation during the course of the experiments because of the application of a DC. On the other hand, on the Al cathode surface, a chemical attack takes place due to the basic pH caused by the water reduction reaction, generating aluminum coagulation species in dissolution [7, 19, 20]. As can be observed, in the

galvanostatic test, for which the highest electric charge was applied, the highest values were obtained for Fe and Al concentrations. Over the course of the experiment, the amounts of Fe and Al increased due to the accumulation of species inside the EC reactor. In other words, the rate of generation of EC species was higher than the rate of elimination in the outflow. In hour 48 of the tests, a purge was carried out because the accumulation of flocs and solid particles inside the reactor hinders the outflow of the treated water. The amount of total coagulant increased linearly with the total charge applied to the EC process. This means that the method of powering the EC is very important and is confirmed with the comparison of the results shown in Figure 6. This figure shows that the process in which the energy supplied to charge the VRFB is double (Scenario c)) obtained results more similar to those obtained in scenario a), although in scenario a) the input of energy was 1/3 higher.

Figure 6. Production of coagulant reagent (■) and ratio Fe/Al (□). a) No use of VRFB; b) powering VRFB with half of the intensity produced in the solar panels; and c) powering the VRFB with 2/3 of the energy provided by the solar panels.

Another important observation is the ratio between iron and aluminum in the coagulant produced. Iron is produced on the anode surface while aluminum is produced on the cathode by chemical corrosion at strongly alkaline pH values. As seen, the powering at constant intensity led to a mixture of coagulant with a higher ratio of iron; this ratio

decreased as the use of the VRFB increased. This observation can be associated to the lower intensity (and hence cell voltage) applied to the cell during the discharge of the VRFB.

Figure 7 shows the way in which the powering affects the treatment performance.

Figure 7. Inlet Dissolved Organic Carbon, DOC (■), outlet Dissolved Organic Carbon, DOC (□) and change in the concentration of Dissolved Organic Carbon, DOC (x) with time. Electrocoagulation of 100 mg dm^{-3} of oxyfluorfen supplied by the current profiles from Figure 4.

The flocs generated by the link of oxyfluorfen micelles and Fe ions decant easily. Therefore, a clarified solution free of pollutant should be generated. However, the results show that removal of oxyfluorfen by enmeshment of the emulsified herbicide on the growing flocs of coagulant was slightly worse in scenario b) and very similar in scenarios a) and c). In spite of the slight improvement in the removal of OFF in scenario a with respect to scenario c), the dose of coagulant used in scenario a) was double that in scenario c) (see Figure 6), which means that the service lifetime of the electrodes in scenario c) will be much longer than in scenario a). Hence, the costs associated with the components of the EC will be lower using the VRFB connected to the EC reactor. Regarding the efficiency of the process, the low value yielded is comparable with that obtained in other pesticide-polluted water EC treatments [8, 9]. It can be confirmed that, although it works, EC is not the best treatment for OFF-polluted wastewater. According to Hakizimana et al., there are a number of parameters affecting EC effectiveness that are related to the operating conditions (current or voltage and operation time), water/wastewater characteristics (pH, alkalinity and conductivity) and geometry of the EC reactor and electrodes (electrode surface, electrode spacing) [7]. Nevertheless, as it was previously studied, we are assessing this treatment in order not to remove, but to

concentrate the pollutant, looking for a more efficient oxidation, as described in our recent paper [3, 21].

Finally, Figure 8 shows the changes observed in pH and conductivity, two of the key parameters used to understand the electrocoagulation process.

Figure 8. Inlet (■) and outlet (□) pH and conductivity with the time. Electrocoagulation of 100 mg dm⁻³ of oxyfluorfen supplied by the current profiles of Figure 4.

No differences were observed in the pH, except for a slightly higher pH in the test carried out with the EC powered by the VRFB. This indicates that the pH increases in the sequence a)<b)<c). Thus, this could explain why in scenario c), the dissolved Al was higher and hence the Fe/Al ratio was close to one, as observed in Figure 6c. Regarding conductivity, the fluctuations between inlet and outlet stream decrease in the case of powering the system at non-constant electric current (scenario b) and are reduced when the action of the VRFB increases. Moreover, this shows that there are no great differences between iron and the aluminum coagulation. On the other hand, the values of conductivity in the outlet stream are slightly lower in the last case. Both facts can be explained in terms of the higher amount of aluminum in the coagulant added when using the VRFB, which was initially unexpected and does not significantly affect the removal of herbicide.

4. CONCLUSIONS

The electrocoagulation of oxyfluorfen wastewater has been carried out under three operation modes:

- Scenario a: the electrocoagulation cell was powered at galvanostatic conditions during days and nights by providing a constant electric current.
- Scenario b: half of the energy produced by solar panels over the sunlight period was used to charge VRFB and the other half to power the electrocoagulation cell. Overnight, the VRFB was connected to the EC until its complete discharge.
- Scenario c: the same as scenario b) but the charge period of the VRFB was performed with double the energy power.

It has been found that electrocoagulation is not suitable for the complete removal of oxyfluorfen from wastewater but attains a significant pollutant accumulation into the flocs of 25%, independent of the mode carried out. Therefore, it can be used as a pretreatment for this kind of waste.

It has been confirmed that an electrocoagulation process can be powered directly with solar energy and that this energy can also be regulated by VRFB in order to provide energy during the night. In the latter case, to achieve the same treatment efficiency, almost 1/3 more energy is required during the energy storage (sunlight) period.

Finally, it is important to note that the use of VRFBs has an impact on the dosing of coagulant. When the system worked with renewable energy coupled to the battery, the electrode dissolution was lower than when a constant current was applied to the system and similar removal efficiencies were achieved. Thus, the use of renewable energy leads to a greater service lifetime of the electrodes, therefore leading also to lower costs associated with the electrochemical reactor.

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