A wind-powered BDD electrochemical oxidation process for the removal of herbicides

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Abstract

In the search for greener treatment technologies, this work studies the coupling of a wind turbine energy supply with an electrolytic cell (CWTEC device) for the remediation of wastewater polluted with pesticide 2,4-dichlorophenoxyacetic acid (2,4-D). The discontinuous and unforeseeable supply of energy is the main challenge inspiring this new proposal, which aims at reducing the environmental impact of electrolytic treatment by using a green energy supply. The results obtained using the coupled technologies are compared with those obtained by powering the electrolyser with a traditional power supply with a similar current intensity. The mineralisation of wastewater can be accomplished independently of how the electrolytic cell is powered, although differences in performance are clearly observed in the total organic carbon (TOC) and 2,4-D decays. These changes can be explained in terms of the changing profile of the current intensity, which influences the concentrations of the oxidants produced and thereby the mediated electrolytic process.

Keywords: Wind turbine, electrolysis, herbicide, boron-doped diamond anode

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1. Introduction

Pesticides exhibit bio-recalcitrant properties and high toxicity and persist in the environment (Wilson et al., 1997). This fact has attracted the interest of the scientific community to develop effective processes to eliminate them from the environment (Fenner et al., 2013; Huang et al., 2011). Among the spectrum of technologies that have been applied to remove or concentrate herbicides from polluted water, it is worth mentioning biological (Megharaj et al., 2011) or membrane processes (Plakas and Karabelas, 2012), adsorption (Nam et al., 2014), advanced oxidation technologies (Ikehata and El-Din, 2006), electrochemical processes (Martínez-Huitle and Brillas, 2009; Rodrigo et al., 2014) and combined technologies (Oller et al., 2011).

For the case of electrochemical-based depletion technologies, anodic oxidation has demonstrated a high ability to completely mineralise a wide range of organic pollutants. In this field, the use of conductive diamond anodes has attracted increasing interest due to their chemical and electrochemical stability and their capability of producing a significant concentration of hydroxyl radicals, a powerful oxidant able to degrade refractory organic pollutants (Brillas and Martínez-Huitle, 2011).

The main operational cost and environmental impact of an electrochemical process for the treatment of polluted water is associated with the use of electricity. A way to minimise this cost and impact is to use a renewable source of energy, which also allows the use of this technology in remote applications, where no grid electricity is available (Bundschuh et al., 2010; Garcia-Segura and Brillas, 2014). Unfortunately, these sources of energy (especially wind energy) are characterised by continuous fluctuations (Carta et al., 2003; de la Nuez Pestana et al., 2004), which usually requires the use of intermediate energy storage components such as batteries. Previous attempts to

evaluate the direct connection of wind power to water treatment systems have focussed on the desalination of brackish waters by membrane technologies (Ma and Lu, 2011; Park et al., 2012; Richards et al., 2014). To the best of the author's knowledge, there are no previous works on the removal of refractory organic pollutants by electrochemical oxidation directly powered by wind energy. However, this combination could be of great interest because of the low impact of the resulting technology.

Based on this background, this work aims to demonstrate the feasibility and usefulness of a coupled wind turbine–electrolytic cell (CWTEC) device operated under actual wind conditions without the assistance of a rack of batteries for the treatment of synthetic wastewater containing the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D). A comparison to the performance of the same electrolytic system powered by a traditional power supply is also carried out to determine if the random distribution of the energy supply can influence the depletion of the pesticide.

2. Materials and methods

2.1 Experimental setup

A Bornay 600 wind power turbine was provided by Bornay Aerogeneradores (Alicante, Spain). The turbine is composed of two fiberglass blades (1 meter long) controlled by an electronic regulator of 24 V and 30 Amp. The regulator acts on the turbines as an automatic overspeed-governing system to keep the rotor from spinning out of control in very high winds. The performance of the wind speed for turn-on is 3.5 m s^{-1} , for nominal power 11.0 m s^{-1} , for the automatic brake system 13.0 m s^{-1} and for work survival 60.0 m s^{-1} .

The electrolyses were conducted in a DiaCell® type 101 supplied by Adamant Technologies (Switzerland). Boron-doped diamond electrodes, BDD (p-Si–boron-doped

diamond) were used as the anode and cathode. The BDD coating has a film thickness of 2 mm, a resistivity of 100 mΩ cm, and a boron concentration of 500 ppm, and the sp³/sp² ratio is 150. The active surface is 70 cm² per compartment, and the interelectrode gap is 3 mm.

2.2 Analysis procedures and methods

The electrooxidation used 4 dm³ of a solution containing 100 mg dm⁻³ 2,4-*D* at natural pH (3.5) and 3.0 g L⁻¹ NaCl as a supporting electrolyte. The electrochemical cell was powered by the wind turbine and with a conventional power supply. In this last case, the experiment was carried out by applying 3.0 A of the external current. The cell reactor was operated in batch-operation mode at a constant temperature, and it was connected by a peristaltic pump (flow rate 26.4 dm³ h⁻¹) to a tank. All of the samples extracted from the electrolysed solutions were filtered with 0.45 μm nylon filters from Whatman before their analysis. Herbicides and aromatic products were monitored by reverse-phase chromatography (Agilent 1100 series, coupled with a UV detector, analytical column Phenomenex Gemini 5 μm C18) and analysed for total organic carbon, TOC (Multi N/C 3100 Analytik Jena analyser).

3. Results and discussion

To assess the performance of the coupled wind turbine-electrolytic cell (CWTEC), a treatment test was planned according to the weather forecast in the area of Ciudad Real by AEMET (the official Spanish Weather Forecasting Service) for a slightly windy day, representing typical conditions, rather than a very windy day, on which the production of energy would be much higher but less representative. Figure 1 shows the wind speed during the test in which the wind turbine powered the electrochemical cell.

As can be observed, there is a random distribution of wind speeds over the testing period with an average wind velocity of 4.2 m s^{-1} . To further characterise the changes in the wind velocity, the inset of Figure 1 shows the distribution of the measured wind velocities, ordered from low to high and classified according to the International Beaufort wind force scale (a well-known reference for classifying wind velocity).

According to this scale, the average conditions of the test could be classified as gentle breeze. As can be observed, approximately 40% of the test was performed under light breeze conditions and another 40% with a gentle breeze. Under light breeze conditions, the production of electricity is expected to be scarce or nil because according to the manufacturer, a minimum wind velocity of 3.5 m s^{-1} is necessary to produce electricity using the wind turbine. At this point, it is important to note that the relationship between the wind velocity and the instantaneous power supplied by the turbine was a highly noisy signal (as expected), although the results were in full agreement with the power curves supplied by provider, confirming the expected productions of energy when the electrochemical system is coupled into the CWTEC device (data not shown). For less than 20% of the day, the wind velocity could be classified into levels 4 and 5 of the International Beaufort wind force scale (moderate and fresh breeze), which are the most interesting conditions for the efficient production of electricity in an inland area such as the place in which the test was carried out. This confirms that the main characteristic of the direct supply of energy from a wind turbine to an electrolytic cell is its discontinuous, random and unforeseeable character, which risks an unsteady production of electricity that will reflect on the results obtained in the treatment of pesticides.

Figure 2 shows the instantaneous current fed to the electrochemical device during the test and the resulting total current electric charge applied to the electrochemical cell during the experiment. As can be observed, the current fed to the system is a direct

function of the wind velocity. As stated above, according to the manufacturer, a minimum wind velocity of 3.5 m s^{-1} is necessary to produce electricity, and this observation is confirmed by the results obtained in the last period of the test in which the wind velocity decreases below this minimum level (light air-calm conditions). During the rest of the test, there can be observed an unforeseeable changing wind velocity, which produced an almost random current intensity profile with respect to time. The total charge passed to the electrolytic system is 18.75 Ah dm^{-3} . This value is much higher than the stoichiometric charge required for the complete oxidation of a 100 mg dm^{-3} solution of 2,4-D (0.36 Ah dm^{-3}).

Fig. 3 shows the concentration of 2,4-D and the total organic carbon (TOC) content with the applied electric charge for the direct connection of the wind turbine to the electrochemical oxidation cell. For the sake of comparison, this figure also shows the results obtained when the electrolytic cell is fed with a conventional power supply in galvanostatic conditions (42.9 mA cm^{-2}) instead of the wind turbine.

As can be observed, the concentration of 2,4-D and TOC content decreased with the applied electric charge, and they are completely depleted in both tests. Moreover, the final average mineralisation efficiency is similar in both cases (1.5% for wind turbine and 1.2% for power supply). However, significant differences can be observed. In the case of the electrolysis fed with the conventional power supply, the decay data follows a typical exponential trend, which is characteristic of the electrolysis of wastewater with a low concentration of pollutants, in which mass transfer limits the overall rate of the process. In the case of the experiment carried out with the renewable energy source, the exponential trend is not as clear. This observation suggests that more complex processes are happening, for which the electrolytic production of oxidants and their role during the treatment could be important and hence not directly related to the charge applied but

also to the reaction time. At this point, it is worth considering that the electrolyte contains chlorides; hence, the production of chlorine, hypochlorite, chlorates and chlorine dioxide and the subsequent mediated oxidation of 2,4-D and intermediates by these oxidants are expected (Canizares et al., 2009; Rodrigo et al., 2010; Sánchez-Carretero et al., 2011). It is also expected that other oxidants such as ozone or hydrogen peroxide are produced, which may help to explain the differences observed.

Another difference arises from the comparison of the 2,4-D and TOC evolution for both systems. In the case of the electrolysis fed with the conventional power supply, the time courses of the decays of TOC and 2,4-D are very similar, suggesting a very low production of intermediates and that 2,4-D molecules that started to be oxidised during the electrolysis are rapidly mineralised. However, in the case of the green energy fed system, the differences between 2,4-D and TOC decay are much higher, suggesting an important production of intermediates. This hypothesis was confirmed by LC-UV, which helps quantify significant concentrations of chlorophenol, hydroquinone and benzoquinone as the main oxidation intermediates. Considering that the same cell and electrodes were used in both tests, the only remarkable change that should explain the differences observed is the changing profile of the operation current density in the system powered with green energy. In the case of the electrolytic system powered with the wind turbine, this current density changes continuously and almost randomly from

0.0 to 243.6 mA cm⁻² depending on the wind velocity, with an average value of 50.0 mA cm⁻², which is only slightly higher than that used when the system is powered with the power supply (15% difference) in galvanostatic mode. The production of oxidants during electrolysis with BDD is known to be strongly dependent on current density (Cañizares et al., 2007). Thus, it is reported that this production is promoted at very high current densities, explaining the large differences in the oxidation of 2,4-D and the time course of the species (Canizares et al., 2009). More research should be performed to clarify this point, but these results are important because they demonstrate that coupling wind turbines to electrochemical cells may lead to different results than those expected for a cell operated at constant current density.

4. Conclusions

The following conclusions can be obtained from the results presented in this work.

- The complete mineralisation of 2,4-D can be achieved when the system is directly fed by a wind turbine, even in non-optimal wind conditions (only 20% of wind force during optimal levels).
- The total applied electric charge required to completely mineralise 2,4-D is similar for both power sources (similar average mineralization efficiency for both power sources). However, there are important differences in the oxidation mechanisms that could be explained in terms of the favoured production of oxidant at very high current densities. Mediated oxidation is favoured in the CWTCE device because of the changing current intensity, and this explains the higher quantity of intermediates.

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Figure captions

Figure 1. Changes in the wind speed during the period of operation of the CWTEC device. Onset: Distribution of wind velocities monitored classified according to the International Beaufort wind force scale.

Figure 2. Instantaneous current and the total applied current charge powered to the electrochemical device.

Figure 3. Decay of 2,4-D concentration (full points) and TOC (empty points) during the electrolyses of a 100 mg dm^{-3} 2,4-D vs. charge applied (Q); (■)wind turbine (▲)conventional power supply. Conditions: initial pH 3, $25 \text{ }^{\circ}\text{C}$, and 3 g dm^{-3} NaCl as supporting electrolyte.

Figure 1

Figure 2

Figure 3