A new strategy for the electrolytic removal of organics based on the adsorption onto granular activated carbon

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Abstract

In this paper, a new strategy for the electrochemical treatment of organics is introduced. It is based on the concentration of the organics by adsorption onto granular active carbon (GAC) with the consequent production of a more highly-concentrated solution of organics in methanol, which is then electrolyzed. Electrolysis in methanol supporting media allows the complete removal of the pollutant and reaction intermediates. A suitable conductivity of the electrolyte was obtained simply by adding sodium hydroxide. Results obtained in the tests carried out in this work show a great improvement in the efficiency of the removal of clopyralid when using this technology, which can lead to very important energy savings. This experiment opens the possibility of using the electrochemical technology more efficiently for the degradation of diluted wastes, which currently is known to be a very inefficient process.

Keywords

Diamond anodes; efficiency, GAC adsorption; non-aqueous electrolytes;

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1. Introduction

For decades, electrolysis with diamond anodes has demonstrated its outstanding performance for the degradation of organic pollutants contained in wastes [1, 2]. This technology is very efficient and, up to now, the only way to improve its performance is its combination with other technologies such as the Fenton oxidation (by the cathodic production of hydrogen peroxide)[3-5] or by the application of ultrasounds or UV light, trying to promote the activation of the oxidants produced in the electrolyte [6-10].

One of the key problems in the electrolytic removal of organics using only electrolysis with diamond is the low efficiency of this technology for the treatment of diluted wastes, which is typically explained in terms of the mass transfer limitations undergone by the electrolytic process[11-13]. These limitations are reflected on the fact that experimental results fit well a first order kinetic. This type of kinetic model indicates that the removal of the same percentage of pollutant requires always the same electric charge regardless of the initial concentration. For example, to remove pollutants from 1000 ppm to 10 ppm (two log units) is required the same electric charge than to remove them from 1.00 to 0.01 ppm (two log units but in a much lower range), despite in the first case it is removed 990 ppm and in the second 0.99 ppm of the pollutant.

Taking into account the very high cost of the electricity, a pre-concentration stage would be very useful in the search of more efficient technologies. This is the goal of several of the research lines that are currently carried out in our Lab, in which we are trying to develop new technologies applicable to the treatment of colloids [14], ionic pollutants [15] and other organics. In this work, we are proposing to combine Granular Activated Carbon (GAC) - adsorption with electrolysis. However, this is not going to be in a direct way as we did in our previous works published at the turn of the century [16, 17], but using methanol as solvent. This is carried out with the aim to improve the total efficiency

of the process, trying to obtain advantage of the different capacities of retention of organic pollutants by GAC in aqueous and methanol media. To do this, first, the different stages of the process are going to be explained and then, a proof of concept of the proposed technology is going to be shown.

2. Materials and methods

2.1. Chemical products.

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) (Sigma Aldrich, Spain) was analytical grade and used as received. Granular Active Carbon (GAC), (Chemviron, Feluy, Belgium) was used as received. Methanol HPLC grade and formic acid (sigma Aldrich, Spain) were used as mobile phase in the HPLC and methanol and double deionized water (Millipore Milli-Q system, resistivity: 8.2M Ω cm at 25 ° C) were used to prepare all solutions.

2.2. Analytical techniques.

The concentration of pesticide and their intermediates generated was followed by reversed-phase chromatography. The chromatography system was an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used. The mobile phase consisted of 30 % methanol/70% water with 0.1 % of formic acid (flow rate: 1 cm³ min⁻¹). The DAD detection wavelength was 280 nm, the temperature was maintained 20°C and the injection volume was 20 μ L.

2.3. Adsorption tests.

Clopyralid stock solutions (100 mg dm⁻³) were prepared dissolving 0.1 g of clopyralid with Milli-Q water and methanol under gentle stirring for 6 hours to assure complete dissolution.

The adsorption capacity of the GAC were tested mixing different quantities of GAC in order to obtain the different isotherms. Experiment was carried out in closed bottles of

100 cm³ placed in an incubating orbital shaker (VWR) with a stirring speed of 180 rpm for 24 hours to guarantee the thermodynamic and kinetic equilibrium.

2.4. Experimental set-up.

To determine the removal efficiency of clopyralid, synthetic electrolytic solution was prepared with 100 mg of the pollutant and 50 mmol of electrolyte (2.925 g of NaCl and 2 g of NaOH) in methanol and water solution (1 dm³). Afterwards, to test the efficiency of the concentration process, minimum volume of pure methanol (0.15 dm³) was mixed with electrolyte and contacted three times with 40g of saturated GAC (50 mg g⁻¹ of GAC). After the extraction processes (3 h stirring at 250 rpm and 30 min in ultrasound bath), the clopyralid solved in methanol was electrolyzed. In addition, same mass quantity of clopyralid (500 mg dm⁻³) in 4.0 dm³ of water was electrolyzed to compare their removal rate and efficiency in both process. The electrolysis were carried out in a cylindrical, undivided, water-jacket glass cell containing 150 cm³ of solution. The headspace above the solution was reduced to the minimum to make it easy collecting the sample with the syringe. In addition, a condenser with circulating water at 25± 1 °C was used to avoid any possible volatile organic compounds (VOCs) to the gas phase. The anode was usually a 3 cm² BDD film (Adamant Technologies, Switzerland), (500 ppm of B, 2.25 µm thickness) and p- type Si as support and graphite of 3 cm² (Carbosystem (Madrid, Spain) was the cathode. The interelectrode gap was 1 cm. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). Current density applied was 250 mA cm⁻² according with typical values studied in previous works [18]. All trials were performed under fast stirring with a magnetic bar to ensure a good mixing and reproducible mass transport conditions.

3. Results and Discussion

The adsorption capacity of granular activated carbon (GAC) depends on the liquid in which the adsorbate is contained. Thus, while GAC has an important affinity for organics and it can be used to retain the pollutants contained in wastewater, its capacity decreases markedly when water is replaced by methanol. For this reason, this solvent is typically used to desorb organics from GAC in particular in Analytical Chemistry labs, where its use is a common practice in the characterization of gaseous samples and in the concentration of liquid samples. This thesis is confirmed in Figure 1, where the isotherms (the amount of solute adsorbed onto the solid (q_e) vs. the equilibrium concentration of the solute in solution (C_e)) at 20°C of clopyralid onto GAC are shown in water and methanol and where it can be observed that the difference in the retention capacity is even higher than two log-units. This means that GAC can be used to retain organic pollutants contained in wastewater and that it can be released into a methanol solution with a lower volume at a much higher concentration.

Figure 1. a) Adsorption isotherms of clopyralid in water (●) and methanol (○) at 20°C
b) Electrolysis of clopyralid solutions in Methanol (■) and water (●) at 250 A m⁻².

The transfer of clopyralid from water to methanol is useless if there is no way to destruct this pollutant in methanol. However, in a previous work of our group [19] we unintentionally found that electrolysis with diamond can destroy organic pollutants in

methanol solutions with a rather good efficiency. In that case, it was only a case of study in which the oxidation of the hormone progesterone was evaluated in methanol because of its low solubility in water. However, Figure 1b shows that it is possible also for clopyralid and that although it is more efficient the degradation in water than in methanol, differences are not excessively large, at least not so large as to impede the combined treatment aimed to be developed in this work. A very important point is that the removal of clopyralid does not mean the combination with methanol but its degradations. Thus, in the HPLC chromatograms obtained during the electrolysis (results not shown) it can be observed the formation of up to four intermediates (methyl carboxylates), which are completely degraded during the electrolysis for electric current charges lower than 35 Ah dm^{-3} . No other intermediates were detected by GC-MS. In addition, it is important to point out that TOC cannot be used in this test to monitor mineralization of the clopyralid because of the huge concentration of methanol (791000 mg $\text{CH}_3\text{OH dm}^{-3}$ corresponding to a TOC of 296625 mg dm^{-3} , which is four log-unit above the TOC associated to clopyralid (TOC of 37.5 mg dm^{-3} corresponding to 100 mg clopyralid dm^{-3}). Initially, this may indicate that methanol could be used cyclically to regenerate the activated carbon, because it does not suffer significant changes and all the species formed from the adsorbate are depleted. Other preliminary results (voltammetric study) also carried out before the tests shown in this work confirmed the extremely low electrochemical reactivity of methanol as compared to clopyralid in solutions of clopyralid in methanol.

In order to demonstrate the feasibility of the technology proposed in this work (proof of concept), 4.0 dm^3 of synthetic wastewater polluted with 500 mg dm^{-3} of clopyralid were treated by direct electrolysis with diamond and by the new combined adsorption-electrolysis process. Part a) of Figure 2 focuses on the adsorption of the pesticide onto the GAC, where it can be seen that there is a very fast rough adsorption in less than two hours,

where the concentration in wastewater decreases from 500 mg dm⁻³ to less than 6 mg dm⁻³. This removal is improved slowly over time in the next 72 h and after this period only 0.7 mg dm⁻³ of clopyralid remains in the wastewater and the rest of the clopyralid is contained in the GAC.

After that, GAC was separated from the wastewater and contacted three times with 0.15 dm³ of methanol (total volume of methanol used 0.45 dm³) for five hours. Concentrations of clopyralid released from the GAC in each of the three consecutive tests are shown in Part b of Figure 2, together with the total amount of clopyralid extracted (1755 of the initial 2000 mg contained in the GAC, which is 87.75%). Hence, the initial problem of 4 dm³ of 500 ppm of clopyralid has been transformed into new problem: 0.45 dm³ (11.25% of the volume) with an average of 3900 mg/L of clopyralid (7.8 times more concentrated).

Figure 2. a) Adsorption of 4 dm³ of 500 ppm of clopyralid onto 40 g of GAC: Δ clopyralid adsorbed onto the GAC, $\diamond$ clopyralid in solution. b) Desorption of 40 g of GAC in three sequential steps with 0.15 dm³ of methanol each ($\bullet$ first desorption test; $\blacksquare$ second desorption test; $\blacktriangle$ third desorption test; $\blacksquare$ total amount of clopyralid released to methanol solution).

Figure 3. Removal of clopyralid during the electrolysis of 4 dm³ of a 500 ppm solution (■) and 0.15 dm³ of a waste processed with GAC concentration onto methanol (●). Onset: comparison of the removal of clopyralid in the three batches of 0.15 dm³ after adding pure methanol to GAC for obtaining high concentrated solutions of clopyralid.

was 718 mg of clopyralid, while with the novel system 741.6 mg can be removed with only 2.6 Ah. Thus, the new strategy is at least 2.4 times more efficient (285.2 vs 113.6 mg/Ah) and this opens to the possibility of using the technology for other different wastes and to improve the sustainability of the electrochemical oxidation processes. At this point, it is worth to indicate that the maximum amount of clopyralid that can be completely oxidized with 1 Ah is 358.13 mg, if 20 electron per molecule are considered for the mineralization (conversion of carbon to carbon dioxide, chlorine to chloride and nitrogen to ammonium).

This means a coulombic efficiency of 79.6% in the case of the new technology, which compares favorably with the 31.7 % achieved with the conventional electrolysis.

The rather low electrochemical reactivity of methanol on diamond anodes as compared to that observed in water supporting electrolytes minimize the possibility of potential side reactions and helps to explain the higher efficiency observed for the new process.

4. Conclusions

From this work, the following conclusions can be drawn:

- Clopyralid can be efficiently concentrated by using GAC adsorption and later desorption in methanol.
- Electrolysis of solutions of clopyralid in methanol allow the complete removal of this pollutant and also the depletion of the reaction intermediates
- Combined GAC adsorption-desorption in methanol and electrolysis of the resulting solution requires much less electrical charge than the treatment of the raw aqueous wastes

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