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

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ABSTRACT

In this paper, a new strategy for the electrochemical treatment of organic pollutants is introduced. This is based on the concentration of 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. 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 could lead to very important energy savings. This experiment opens the possibility of using electrochemical technology more efficiently for the degradation of diluted wastes, which is currently a very inefficient process.

1. Introduction

For decades, electrolysis with diamond anodes has demonstrated 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 has been by combination with other technologies such as Fenton oxidation (by the cathodic production of hydrogen peroxide) [3–5] or by the application of ultrasound or UV light, with the aim of promoting 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 by the fact that the experimental results are a good fit for first-order kinetics. This type of kinetic model indicates that the removal of the same percentage of pollutant requires the same electric charge, regardless of the initial concentration. For example, to reduce pollutants from 1000 ppm to 10 ppm (two log units) requires the same electric charge as to reduce them from 1.00 to 0.01 ppm (two log units but in a much lower range), despite the fact that in the first case 990 ppm and in the second 0.99 ppm of the pollutant is removed.

Taking into account the very high cost of electricity, a pre-concentration stage would be very useful in the search for more efficient technologies. This is the goal of several lines of research currently being carried out in our laboratory, where we are trying to develop new technologies applicable to the treatment of colloids [14], ionic pollutants [15] and other organics. In this work, we propose to combine adsorption onto Granular Activated Carbon (GAC) with electrolysis. However, this is not achieved directly, as in our previous works published at the turn of the century [16,17], but using methanol as solvent. This is done with the aim of improving the total efficiency of the process, trying to take advantage of the different capacities for retention of organic pollutants of GAC in aqueous and methanol media. In this paper we will first explain the different stages of the process and then provide a proof of concept of the proposed technology.

2. Materials and methods

2.1. Chemical products

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) (Sigma Aldrich, Spain) was of 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 the mobile phase in the HPLC and methanol and double deionized water (Millipore Milli-Q system, resistivity: 8.2 MΩ cm at 25 °C) were used to prepare all solutions.

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2.2. Analytical techniques

The concentration of pesticides and their generated intermediates was followed by reverse-phase chromatography. The chromatography system was an Agilent 1200 series coupled to 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 $cm^3\ min^{-1}$). The DAD detection wavelength was 280 nm, the temperature was maintained at 20 °C and the injection volume was 20 μL.

2.3. Adsorption tests

Clopyralid stock solutions (100 mg dm^{-3}) were prepared by dissolving 0.1 g of clopyralid in Milli-Q water and methanol under gentle stirring for 6 h to ensure complete dissolution.

The adsorption capacity of the GAC was tested by mixing different quantities of GAC in order to obtain different isotherms. Experiments were carried out in closed bottles of 100 cm^3 placed in an incubating orbital shaker (VWR) with a stirring speed of 180 rpm for 24 h to guarantee thermodynamic and kinetic equilibrium.

2.4. Experimental set-up

To determine the removal efficiency of clopyralid, a 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 dm^3). Afterwards, to test the efficiency of the concentration process, a minimum volume of pure methanol (0.15 dm^3) was mixed with electrolyte and contacted three times with 40 g of saturated GAC (50 mg g^{-1} of GAC). After the extraction processes (3 h stirring at 250 rpm and 30 min in an ultrasound bath), the clopyralid dissolved in methanol was electrolyzed. In addition, same mass quantity of clopyralid (500 mg dm^{-3}) in 4.0 dm^3 of water was electrolyzed to compare the removal rate and efficiency in both processes. The electrolyses were carried out in a cylindrical, undivided, water-jacket glass cell containing 150 cm^3 of solution. The headspace above the solution was reduced to the minimum to make it easy to collect the sample with the syringe. In addition, a condenser with circulating water at 25 ± 1 °C was used to avoid the loss of any possible volatile organic compounds (VOCs) to the gas phase. The anode was usually a 3 cm^2 BDD film (Adamant Technologies, Switzerland) (500 ppm of B, 2.25 μm thickness) and p-type Si as support with a 3 cm^2 graphite (Carbosystem (Madrid, Spain) cathode. The interelectrode gap was 1 cm. The electric current was provided by a Delta Electronika ES030–10 power supply (0–30 V, 0–10 A). The current density applied was 250 mA cm^{-2}, which is a typical value studied in previous works [18]. All trials were performed under fast stirring with a magnetic bar to ensure 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 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 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 Fig. 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)) for clopyralid and GAC at 20 °C are shown in water and methanol. 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.

The transfer of clopyralid from water to methanol is useless if there is no way to destroy this pollutant in methanol. However, in a previous work [19] we unintentionally found that electrolysis with diamond can destroy organic pollutants in methanol solutions with a rather good efficiency. In that case, the oxidation of the hormone progesterone was being evaluated in methanol because of its low solubility in water. However, Fig. 1b shows that this is also possible for clopyralid and that although the degradation in water is more efficient than in methanol, the differences are not excessively large, at least not so large as to impede the combined treatment proposed in this work. A very important point is that the removal of clopyralid does not mean its combination with methanol but its degradation. Thus, in the HPLC chromatograms obtained during the electrolysis (results not shown) the formation of up to four intermediates (methyl carboxylates) can be observed, 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 (791,000 mg $CH_3OH\ dm^{-3}$ corresponding to a TOC of 296,625 mg dm^{-3}, which is four log-units above the TOC associated with clopyralid (TOC of 37.5 mg dm^{-3} corresponding to 100 mg clopyralid dm^{-3}). 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 studies) also carried

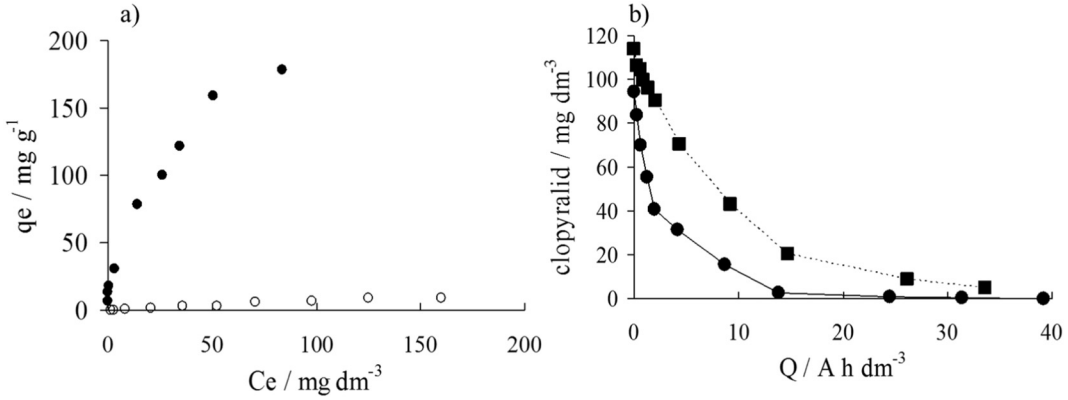

Fig. 1. (a) Adsorption isotherms of clopyralid in water (●) and methanol (○) at 20 °C (b) Electrolysis of clopyralid solutions in methanol (■) and water (●) at 250 A m^{-2}.

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