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Study of an Air Diffusion Activated Carbon Packed Electrode for an Electro-Fenton Wastewater Treatment

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ABSTRACT

An air diffusion activated carbon packed electrode was used to promote the *in-situ* generation of hydrogen peroxide (H_2O_2) to support an electro-Fenton based method for the degradation of a typical dye, Methyl Orange (MO) at two different concentrations in an aqueous effluent ($250\,mg\,L^{-1}$ and $97\,mg\,L^{-1}$). Electrochemical experiments were carried out using a one compartment cylindrical cell with granular activated carbon (GAC) configured as an air diffusion cathode. The efficiency of the electrode was explored as a function of H_2O_2 produced reaching a maximum value of 10 mM. Experimental parameters such as applied current (300, 200, 100 and 50 mA), initial Fe^{2+} concentration (0.2, 0.5 and 0.8 mM) and electrode stability (10 cycles) were studied. High Total Organic Carbon (TOC) decay (90%) and color removal (100%) were obtained using this electrode under appropriate operation conditions. Consecutive degradation cycles of electro-Fenton process were performed in the electrochemical cell without great loss of the removal efficiency. Considering that, in the proposed packed electrode, the use of air diffusion GAC as cathode results in efficient degradation and cost reduction for the conventional electro-Fenton process, this electrode approach could constitute an excellent alternative for H_2O_2 generation when compared to conventional carbon electrodes.

1. Introduction

Several research groups had made important efforts to develop appropriate treatment processes to remove organic matter of wastewaters from the textile industry [1]. Nowadays, various advanced oxidation processes such as electrochemical oxidation [2,3], photocatalytic oxidation [4], Fenton, electro-Fenton and photoelectro-Fenton [5–11] have been proposed as promising environmental remediation technologies. In this regard, there has been an increasing interest in the use of *in-situ* electrogenerated hydrogen peroxide by means of oxygen reduction in Fe^{2+} containing acidic solutions in order to develop electro-Fenton processes to treat wastewater [12–15]. In this technology development approach, the role of the cathodes is crucial to achieve an efficient production of H_2O_2, and therefore, attention has focused on the investigation of carbon-based materials such as graphite [12,16], reticulated vitreous carbon [17], nitrogen functionalized carbon nanotubes [18], carbon sponges [19], activated carbon fiber [20] or gas diffusion electrodes [21–24].

Although graphite is by far the most popular carbon electrode choice due to its low cost, poor oxygen solubility in aqueous medium coupled to mass transfer limitations cause low efficiencies. On the other hand, gas-diffusion cathodes increase the surface concentration of oxygen and reduce mass transfer limitations but their size and surface area is commonly small, adding up to high cost and instability for long term operation [25]. A new type of electro-Fenton process based on the Pd-catalytic production of H_2O_2 from electro-generated H_2 and O_2 also has been reported by Yuan et. Al. [26,27] and Liao et. Al. [28]. This new type of electro-Fenton process also increases the surface concentration of oxygen and reduces mass transfer limitations.

Our research group [29] recently studied the adsorption regeneration of a granular activated carbon (GAC) packed electrode previously loaded with toluene using an electro-Fenton-based method. The results showed an adsorption regeneration capacity

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for GAC of about 90% after ten cycles of treatment. Since the main limitation of this approach relied on the low oxygen solubility and the poor mass transfer, an air bubbling approach on the particles of GAC packed bed electrode led us to expect an increase on the availability of O_2 for the reduction reaction, and an improved mass transfer of dissolved oxygen and electrogenerated H_2O_2, that in turn, should increase the efficiency of an electro-Fenton process [30]. In this way, this work investigates the influences of some operation parameters and electrolytic conditions such as applied current and Fe^{2+} concentration on TOC and % color removal of a wastewater polluted with a dye model (Methyl Orange, MO).

2. Experimental

2.1. Chemicals

Analytical grade Methyl Orange was purchased from UCB. Anhydrous sodium sulfate and ferrous sulfate heptahydrate were supplied by Panreac. The electrolytic solution was prepared with deionized water (Millipore Milli-Q, 18 MΩ cm), and its pH was adjusted to 3.0 with analytical grade sulfuric acid from Merck. GAC was obtained from Panreac with an average grain size of 3-5 mm. A Brunauer – Emmett – Teller (BET) (N_2) specific surface area of 850 m^2/g, a pore volume of 1.0 cm^3/g and a 15% residue on ignition at 600° C characterize this material.

2.2. Electrolytic System

All electrolytic experiments were performed with an open, one compartment cylindrical cell of 150 mL, equipped with a double jacket chamber for circulation of external thermostated water to regulate the solution' temperature. The temperature was adjusted with a Thermo Electron Corporation HAAKE DC 10 thermostat as can be seen in Fig. 1.

The cell was also equipped with a 3 cm^2 boron-doped diamond (BDD) thin film anode purchased from Adamant Technologies (La-Chaux-de- Fonds, Switzerland) and with a GAC air-diffusion cathode separated from the anode by a distance of about 1 cm. The cathode was mounted replacing the carbon cloth described in [31] with 1 gram of granular activated carbon. In order to obtain good conductivity, GAC was packed and compacted within the tubular support and connected by Ni/Cr wire as can be seen in Fig. 1. The GAC cathode was fed with continuously pumped air to generate H_2O_2. All the experiments were made under constant current operation conditions provided by an Amel 2049 potentiostat–galvanostat. Before using the electrodes, the anode was polarized in 0.05 M Na_2SO_4 solution of pH 3 at 100 mA cm^{-2} for 240 min, to remove the impurities of the BDD surface. The GAC cathode on the other hand, was washed several times with distilled water and dried in a stove at 110 °C. The solutions were kept at 25 °C, and during the experiment were stirred with a magnetic bar at 800 rpm to ensure mixing and transport of reactants towards/from the electrodes.

2.3. Apparatus and analytical procedures

The solution pH was measured with a Crison GLP 22 pH-meter. Aliquots withdrawn from the electrolyzed solutions were neutralized and filtered with 0.45 μm PTFE filters obtained from Whatman before analysis. The mineralization of MO solutions was monitored from their TOC decrease, measured with a Shimadzu VCSN total organic carbon analyzer. From these data, the mineralization current efficiency (MCE) at a current I (A) and time t (h), was estimated as follows [32]:

$$MCE(\%) = \frac{nFV_S\Delta(TOC)\,\mathrm{exp}}{4.32 \times 10^7 mIt} \times 100 \quad (1)$$

where F is the Faraday constant (96,487 C mol^{-1}), V_s is the solution volume (L), Δ(TOC) is the experimental TOC decay (mg L^{-1}), t, is time, I, is current (A), 4.32×10^7 is a conversion factor to homogenize units (3600 s h^{-1} × 12,000 mg mol^{-1}) and m is the number of carbon atoms of methyl orange (14 atoms). The number of electrons (n) consumed per each molecule was taken as

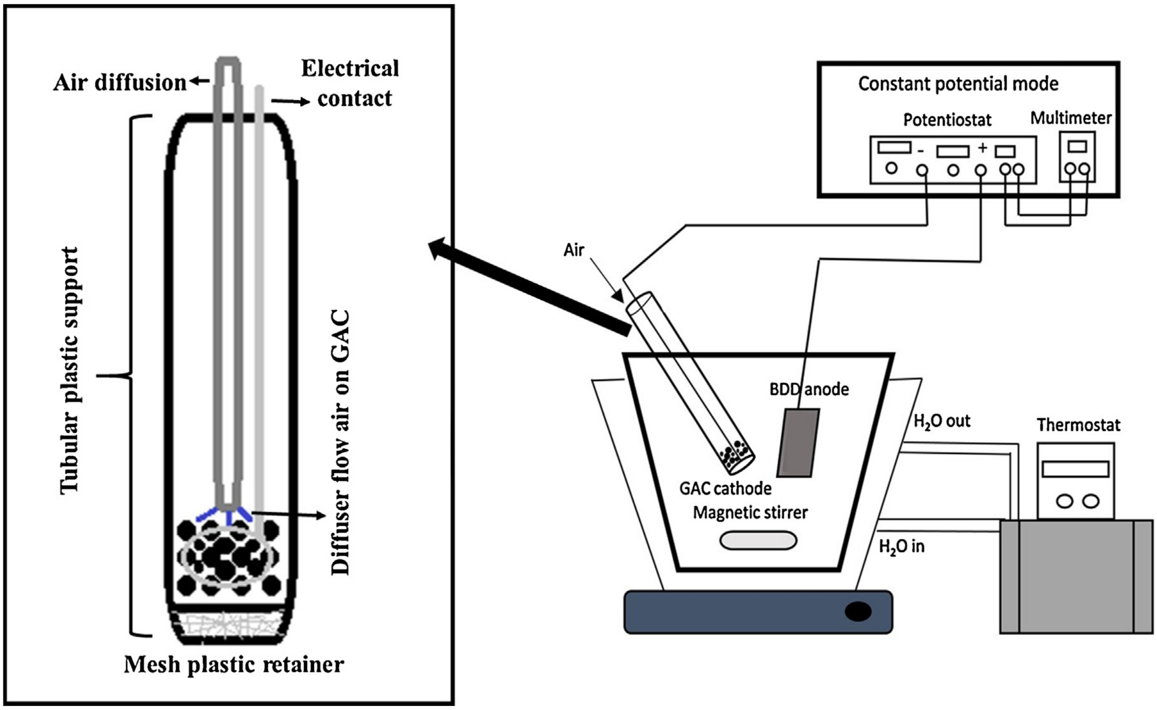

Fig. 1. Schematic representation of the electrolytic system used for electrochemical experiments.