



Facile Preparation of Porous Carbon Cathode to Eliminate Paracetamol in Aqueous Medium Using Electro-Fenton System



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ABSTRACT

Porous carbon cathode (PCF) was fabricated by thermal treatment at high temperature under a nitrogen gas flow mixed with 1% of oxygen. Scanning electron microscopy results revealed a homogenous porosity covered the carbon fibres. This property improved significantly the hydrophilicity that supported the oxygen reduction reaction (ORR) in electro-Fenton process as confirmed by contact angle measurements. In addition, an increase of 700 times of the surface area is observed after the thermal treatment. The crystalline average size of the new material was also ameliorated during thermal treatment as observed by X-ray diffraction pattern (XRD) due to the selective etching of amorphous carbon. Porous cathode exhibited also better electrochemical performances than raw carbon felt cathode as proved by cyclic voltammograms (CVs) because of the higher electroactive surface area. According to the Randles-Sevcik formula, the electroactive surface area of PCF was 10 times higher than raw CF. The concentration of H₂O₂ on PCF and raw CF was 24.6, 7.9 mg L⁻¹ respectively after 80 min. The porous cathode was applied for removal of paracetamol (PCM) in acidic aqueous medium using an electro-Fenton process. Mineralization of PCM was followed by total organic carbon (TOC) measurements and an improvement of 31% was observed compared to the non-modified cathode after 2 h of electrolysis. The porous carbon cathode kept its stability after 10 cycles.

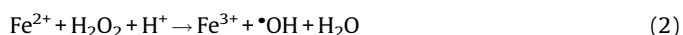
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1. Introduction

Among Advanced Oxidation Processes (AOPs) technologies like ozonation [1], UV/H₂O₂ [2] or photocatalytic oxidation [3], the electro-Fenton process has a high potential to ensure the mineralization (conversion into CO₂ and H₂O) of organic pollutants and micropollutants. In the process, powerful oxidant hydroxyl radicals (•OH) are produced in an electrochemically assisted Fenton's reaction involving hydrogen peroxide (H₂O₂) and ferrous iron, according to the following reaction: [4].



Since this reaction takes place in acidic medium, it can alternatively be written as:



H₂O₂ is formed via the two-electrons oxygen reduction reaction (ORR) at the cathode:



Carbon-based materials are the best electrode used as a cathode in the electro-Fenton (EF) system. Different kinds of carbon based materials have been investigated: Carbon sponge cathode has been used in order to mineralize basic blue 3 (BB3) dye in water with efficiency of 50.8% higher than the carbon cathode after eight hours of electrolysis. 91.6% of TOC removal has been observed in the end of the process. [5] Polyacrylonitrile-based carbon fiber brush cathode has been as well investigated. It shows an efficiency of 86.2% of COD removal of phenol. The same cathode has been used for the mineralization of the complex real dyeing wastewater (Taiwan) with 70% of COD removal after 240 min of treatment [6]. Elisabetta et al. demonstrated that carbon felt (CF) and reticulated vitreous carbon (RVC) were more effective than graphite cathode in the H₂O₂ electrogeneration by electro-Fenton process [7].

In fact, the production of hydrogen peroxide is a crucial factor for the effective destruction of Persistent Organic Pollutants (POPs) by EF process. Oxygen gas is dissolved in the aqueous phase and sequentially transferred from the bulk to the cathodic surface, where it is reduced to hydrogen peroxide [8]. The efficiency of EF process was mainly limited by low mass transfer kinetics of hydrogen peroxide to the cathode due to the low solubility of

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oxygen or mislaying of H₂O₂ from its anodic oxidation via HO₂• as an intermediate through the following reactions [9]:



To minimize problems, the process can then be optimized by using gas diffusion cathode [10] rotating cathode to optimize diffusion [11] or divided cell to avoid H₂O₂ oxidation at the anode [12]. Otherwise, there are also many studies focus on the modification of cathode materials to raise the electrogeneration of hydrogen peroxide though (i) the improvement of the electroactive surface area, and (ii) the hydrophilic property in order to accelerate the electron transfer of O₂ reduction achieving higher mass transfer rate and to increase the reaction rate between H₂O₂ and the catalyst to decline the anodic oxidation. The modification of carbon felt for instance by ethanol/hydrazine hydrate shows a mineralization ratio on p-nitrophenol (p-Np) of 51.4% after 120 min electrolysis, more than 2 times of the pristine one [13]. The modification of the same carbon felt by graphene demonstrated a 73.9% TOC removal of Acid Orange 7 dye after 2 h treatment, which was 18.3% higher than on the raw carbon felt [14]. The deposition of carbon black and polytetrafluoroethylene (PTFE) on graphite felt could increase the in situ production of H₂O₂ by about 10.7 times [15], where the deposition of nitrogen functionalized carbon nanotube could increase the concentration of H₂O₂ by about 1.6 times in comparison to the non-modified electrodes. [16] Finally, the modification of the electrode by multi-walled carbon nanotubes/surfactant [17] or/and by polypyrrole/anthraquinone-disulphonate composite film [18] attained also better results than the non-modified cathodes.

Paracetamol (N-(4-hydroxyphenyl) acetamide) is widely used in pharmaceutical field and has been known as a recalcitrant compound very difficult to remove completely [19]. This drug is detected in European sewage treatment plant (STP) with a concentration of 6 µg/L [20], up to 10 µg/L in water natural resource in USA [21] and over than 65 µg/L in the Tyne River, UK [22]. By increasing the usage of paracetamol yearly in the world, more amounts of pharmaceuticals enter the environment from manufacturing wastes which can produce toxic effects to aquatic organisms [23]. The Fenton process has been used as an efficient method to degrade the drug paracetamol from water. By the catalytic action of Fe²⁺, Cu²⁺, and UVA light on electrogenerated hydrogen peroxide, Sire's et al. had totally mineralized paracetamol after 6 h treatment, and some by-products formed during the electrolysis were detected like hydroquinone, p-benzoquinone, or short chain carboxylic acids [24]. In addition, acetaminophen was also removed by the combination between electro-Fenton and photoelectro-Fenton processes in a double cathodes electrochemical cell [25], by coupling of adsorption and photo-Fenton using nanozeolites and cobalt ferrite nanoparticles [26], by bioelectrochemical degradation in a microbial fuel cell-Fenton system [27], and finally by other methods relevant to the photo-Fenton process [28–31]. From that, the improvement of Fenton process to upgrade the treatment efficiency of recalcitrant pharmaceutical drugs is necessary as well as brings the enormous benefits for human living environment.

In this study, we prepared porous cathode from carbon felt by thermal treatment. This cathode was used to decompose PCM because that the improvement of the electroactive surface area after modification assisted the oxygen reduction reaction (ORR) to increase the H₂O₂ generation. Moreover, the porous morphology ameliorated remarkably the hydrophilicity of the raw carbon felt. Dissolved oxygen in the solution was moved quickly and easily to

be reduced at the modified cathode. From that, the efficiency of the electro-Fenton process was improved and PCM mineralization was enhanced.

2. Experimental

2.1. Materials

The carbon felt was purchased from Johnson Matthey Co., Germany. Paracetamol (acetaminophen), sodium sulphate (anhydrous, ≥99%) and iron (II) sulphate hepta-hydrate (99%), were obtained from Sigma-Aldrich. Potassium hexacyanoferrate (≥99%) and potassium nitrate (≥99%) were bought from Fluka. TOC standard of 1000 mg/L (Sigma-Aldrich Co) and sodium hydrogen carbonate (≥99.5%, ACS, Karlsruhe) were used for calibration. Potassium titanium (IV) oxalate (99.99%, Alfa Aesar), and potassium permanganate (>99%), acid sulfuric (95–97%), standard hydrogen peroxide solution (≥30% w/w) from Sigma-Aldrich were used for the hydrogen peroxide accumulation determination with time.

2.2. Preparation of porous carbon felt

The commercial carbon felt with a dimension of 5.0 cm × 1.0 cm × 1.27 cm was first cleaned in an ultrasonic bath with acetone for 2 h to remove adsorbed contaminations, followed by thorough rinse with deionized water and dried at 60 °C for 24 h. This pretreated carbon felt was denoted as raw CF. After that, these carbonaceous samples were thermal treated in a tubular furnace (Vecstar Ltd), feeding by a mixture N₂/O₂ with 1% of oxygen. To obtain the optimal condition, experiments were performed under various parameters such as different treatment temperatures and times through keeping constantly the income gas flow at 200 mL/min. The sample at the best state was noted as Porous Carbon Felt (PCF).

2.3. Material Characterization

Chemical and structural characterizations have been performed using a scanning electron microscopy (SEM, Hitachi S-4800), a homemade contact angle meter, and a X-ray diffraction (PANalytical Xpert-PRO diffractometer equipped with a X'celerator detector using Ni-filtered Cu-radiation). The crystallite size was obtained from the X-ray diffraction pattern using of the Scherrer's formula [32].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (4)$$

Where D is the grain size (Å), k is a constant equal to 0.94, β is the full width at half maximum (FWHM) (radian) and λ (Å) is the wavelength of the X-rays.

The N₂ sorption-desorption isotherms were measured with a Micromeritics ASAP 2010 equipment (outgassing conditions: 200 °C-12 h).

Electrochemical characterization was investigated relying on cyclic voltammograms (CVs). Experiments were conducted in solution of 10 mM K₃[Fe(CN)₆] and 1.0 M KCl by using the µ3AUT70466 Autolab system (Eco Chemie BV, Netherlands) and Bio-Logic SP-150 in a three-electrodes cell including a working electrode (modified and unmodified CF), a counter electrode (Pt foil), and a reference electrode (Saturated Calomel Electrode, SCE). The electroactive surface area of cathodes was calculated according to the Randles-Sevcik formula [33,34].

$$Ip = 2.69 \times 10^5 \times AD^{1/2} n^{3/2} \gamma^{1/2} C \quad (5)$$

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