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

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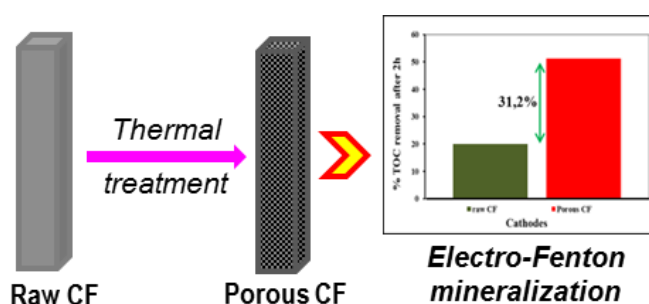
ABSTRACT

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 2h of electrolysis. The porous carbon cathode kept its stability after 10 cycles.

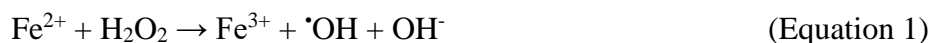
KEYWORDS. Porous carbon felt, water treatment, electroactive surface area, mineralization, hydrogen peroxide production, electro-Fenton reaction

GRAPHICAL ABSTRACT



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 (\bullet 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:

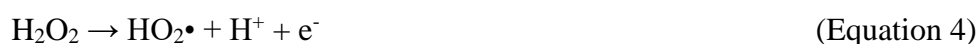


H₂O₂ is formed via the two-electrons oxygen reduction reaction (ORR) at the cathode:



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 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 2h 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/ anthraquinonedisulphonate 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, Sirés *et al.* had totally mineralized paracetamol after 6h 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 bio-electrochemical 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, $\geq 99\%$) and iron (II) sulphate hepta-hydrate (99%), were obtained from Sigma-Aldrich. Potassium hexacyanoferrate ($\geq 99\%$) and potassium nitrate ($\geq 99\%$) were bought from Fluka. TOC standard of 1000 mg/L (Sigma-Aldrich Co) and sodium hydrogen carbonate ($\geq 99.5\%$, 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 ($\geq 30\%$ 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 x 1.0 cm x 1.27 cm was first cleaned in an ultrasonic bath with acetone for 2h to remove adsorbed contaminations, followed by thorough rinse with deionized water and dried at 60⁰C for 24h. 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].

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

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-12h).

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].

$$I_p = 2.69 \times 10^5 \times AD^{1/2}n^{3/2}\nu^{1/2}C \quad (\text{Equation 5})$$

Where n is the number of electrons participating in the redox reaction, A is the area of the electrode (cm²), D is the diffusion coefficient of the molecule in solution (cm².s⁻¹), C is the

concentration of the probe molecule in the bulk solution (mol cm^{-3}), and γ is the scan rate of the potential perturbation (V s^{-1}).

2.4. Electrogeneration of hydrogen peroxide

Hydrogen peroxide concentrations were determined by spectrophotometry using the potassium titanium (IV) oxalate as a colored indicator. The absorbance of the yellow pertitanic acid complex between hydrogen peroxide and potassium titanium oxalate in acid solution was measured by a Spectrophotometer Jenway 6300 (Barioworld Scientific Ltd, Dunmow UK) at $\lambda = 400$ nm through a 10 mm quartz cuvette. The calibration curve was contributed from standard hydrogen peroxide solution which was titrated by potassium permanganate solution (0.1N). Electrogeneration of H_2O_2 was carried out in the undivided two-electrodes cell with platinum foil as anode and carbon felt as cathode containing 30mL solution of Na_2SO_4 (50 mM, pH =3) under saturating of oxygen.

2.5. Mineralization of paracetamol by the EF process

The electro-Fenton treatment of paracetamol (PCM) aqueous solution was carried out in a 75 mL undivided two-electrodes cell using a stabilized alimentation (Lambda Electronique, USA) to control the applied current. The prepared cathode (2 cm^2) was used as working electrode and a platinum foil as counter electrode. The distance between the working electrode and the counter electrode was 3 cm. The 30 mL aqueous solution of PCM (0.1 mM) and Na_2SO_4 (50 mM) as supporting electrolyte and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.2 mM) as the catalyst were prepared by adjusting pH at 3. Prior to the electrolysis, oxygen was bubbled to saturate the solutions which were stirred magnetically at 800 rpm. The total organic carbon (TOC) of the initial and treated samples was measured with a TOC-L CSH/CSN Shimadzu (Japan) analyzer. Calibration curves for total carbon (TC) and inorganic carbon (IC) analysis were built up by automatic dilution of standards solutions of TOC (potassium hydrogenophthalate) and IC (sodium hydrogen carbonate).

3. Results and discussion

3.1. Chemical and structural characterizations of porous carbon cathode

Figure 1a and 1b illustrated the SEM images of the raw Carbon Felt (CF) and Porous CF (PCF) obtained by thermal treatment at 1000⁰C for 1h under a nitrogen flow mixing with 1% oxygen. It was observed that the morphology of raw CF was very smooth without any porous structure compared to PCF. Therefore, CF owned a very low surface area around 0.09 m²/g (Table 1) attributed to a non-porous system. In contrast, the surface of PCF was very rough and filled up by many holes. As the result of thermal treatment by gas flow containing 1 % oxygen under high temperature, the upgraded surface area was identified to be 63.88 m²/g and the pore volume is calculated to be 0.0707 cm³/g (Table 1) which was 700 times higher than the raw CF. The contact angle of the modified sample was 0° instead of 89.9° on the bare one (Figure 1c, d) because of the fast water droplets absorption by this porous structure. This higher surface hydrophilicity was helpful to enhance the production of hydrogen peroxide from the dissolved oxygen adsorbed at the surface of cathode in electro-Fenton process [35, 36]. In addition, the increase of the surface area could promote the electron transport and the mass transfer between the cathode and the electrolyte, which was proved by the enhancement of the electrocatalytic behavior as showed later with cyclic voltammograms (CVs) (Figure 1f).

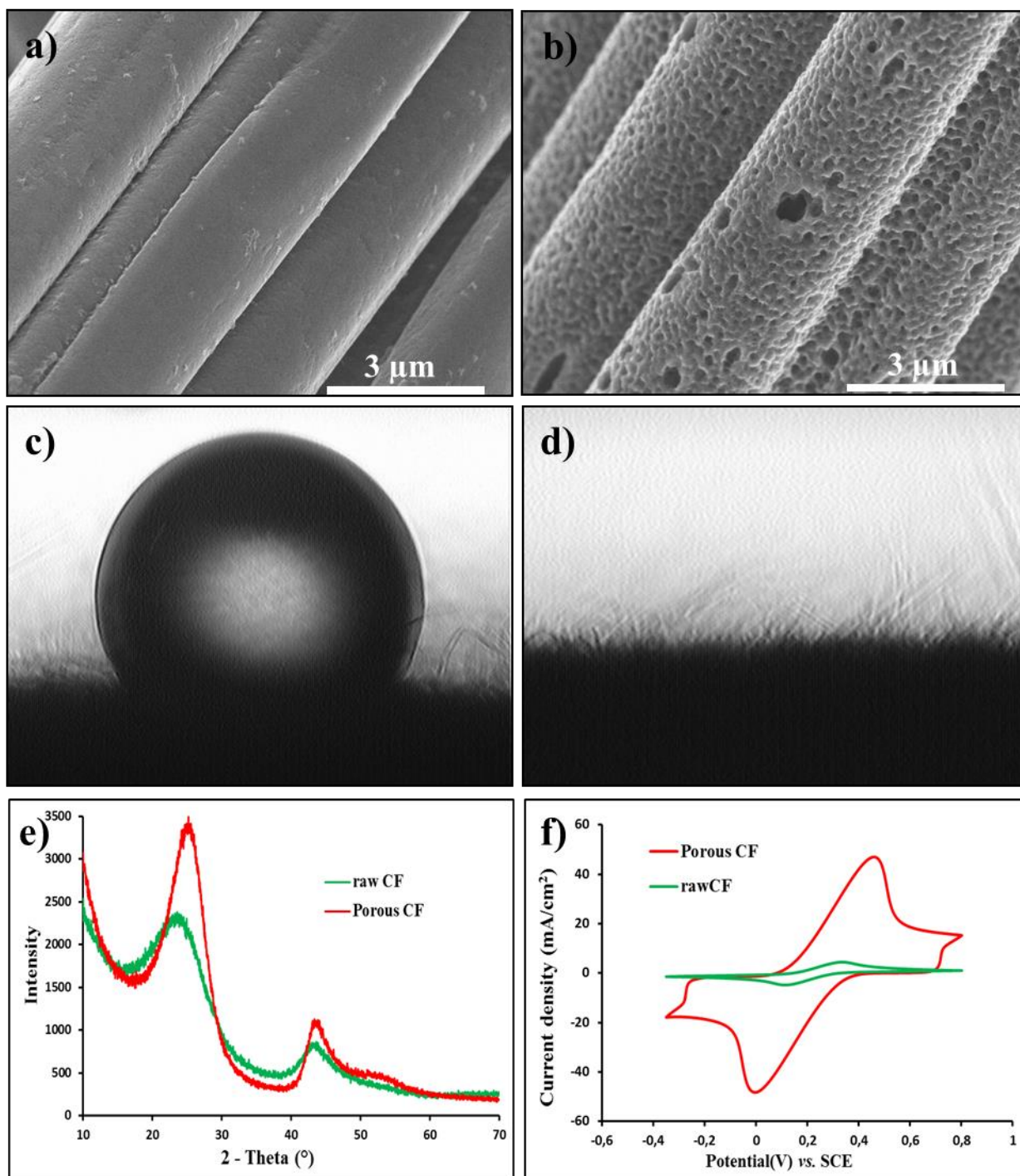


Figure 1. SEM images of (a) raw carbon felt (raw CF) and (b) Porous carbon felt (PCF) after thermal treatment at 1000°C for 1h under nitrogen flow mixing with 1% oxygen. Shapes of water droplets formed on (c) raw CF and (d) Porous carbon felt. (e) X-ray diffraction patterns of raw CF and Porous CF, and (f) Cyclic voltammograms (CVs) in potassium hexacyanoferrate solution at scan rate 7 mV/s of raw CF and Porous CF.

Table 1. Surface area and porosity of carbon felt for different thermal treatments under a nitrogen gas flow mixed with 1% of oxygen.

| | raw CF | CF-600°C/1h | CF-800°C/1h | CF-1000°C/1h | CF-1000°C/3h |
|---------------------------------------|--------|-------------|-------------|--------------|--------------|
| Surface Area (m²/g) | 0.09 | 1.37 | 12.11 | 63.88 | 2.91 |
| Pore Volume (cm³/g) | - | 0.0016 | 0.0086 | 0.0707 | 0.0041 |
| Pore Size (Å) | - | 22.1 | 28.9 | 32.5 | 42.2 |

The crystalline average size of the material was also improved during the thermal treatment. The crystallite size obtained from the X-ray diffraction pattern (Figure 1e) was calculated by Scherrer's formula. For PCF and raw CF, values are 13.5 Å and 12.7 Å respectively (Table 2). This increase of the crystal size average is related to the fact that at high temperature (1000°C), the amorphous and turbostratic carbon would be oxidized first by the reaction with oxygen in the oven and the more crystallite (graphitic) carbon remained which would increase the average of the crystalline size. In fact, owing to much more defects existing in the amorphous carbon, oxidation would be more reactive toward the amorphous carbon and turbostratic carbon than the graphitic carbon. This selective etching due to the fact that amorphous carbon can be etched away more easily (faster oxidation reaction), will induce the increase in the surface area and the appearance of the porosity in the PCF [37].

To investigate the effect of thermal treatment on the electrochemical activity of cathodes, cyclic voltammograms were shown in Figure 1f. It could be seen that PCF resulted in larger current response toward $[\text{Fe}(\text{CN})_6]^{3-/4-}$ when compared to raw CF in the scan range between 0.8V and -0.35V/ECS. The porous surface as well as the improved hydrophilicity enhanced the electron-transfer efficiency, leading to the expansion of electroactive surface area on PCF. Electroactive surface area was calculated from the Randles-Sevcik formula and was 586.44 cm²/g for PCF, 10 times higher than raw CF (62.16 cm²/g).

Table 2. Crystallite size and electroactive surface area of carbon felt for different thermal treatments under a nitrogen gas flow mixed with 1% of oxygen.

| | raw CF | CF-600°C/1h | CF-800°C/1h | CF-1000°C/1h | CF-1000°C/30' | CF-1000°C/2h | CF-1000°C/3h |
|--|--------|-------------|-------------|--------------|---------------|--------------|--------------|
| Crystallite size (Å) | 12.7 | 13.0 | 13.2 | 13.5 | 13.4 | 12.9 | 12.4 |
| Electroactive surface area (cm²/g) | 62.16 | 461.64 | 524.03 | 586.44 | 536.50 | 486.60 | 349.35 |

3.2. Effect of the thermal treatment temperature

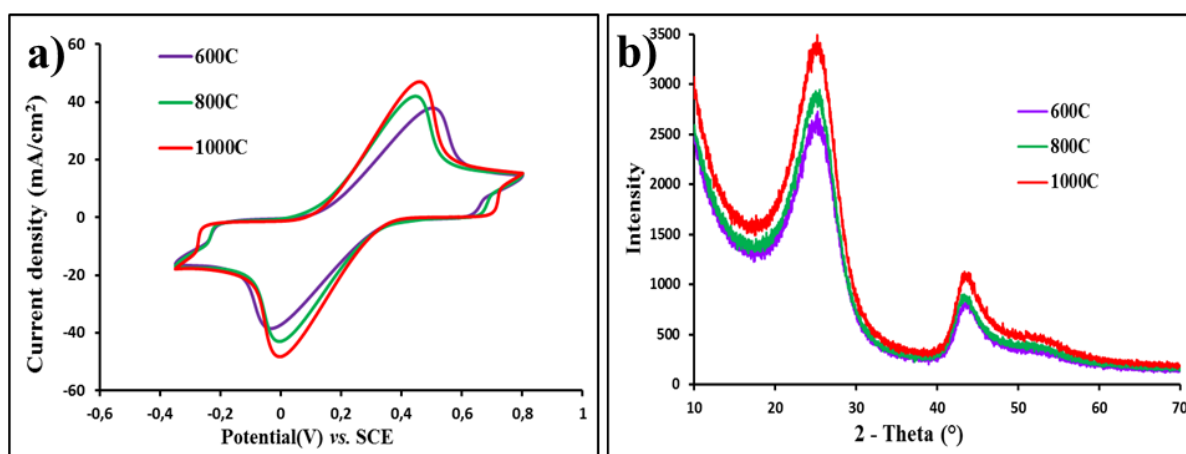


Figure 2. (a) Cyclic voltammograms (CVs) in potassium hexacyanoferrate solution at scan rate 7 mV/s, and (b) X-ray diffraction patterns of electrodes treated at different thermal temperatures in 1h under nitrogen flow mixing with 1% oxygen.

Figure 2 presented cyclic voltammograms and XRD patterns at different temperatures of treatment. The peak current of the redox probe $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ increased as the temperature climbed from 600°C up to 1000°C. The average crystallite size increased with the increase of calcination temperature: 13.0, 13.2 and 13.5 (Å) for 600, 800 and 1000°C respectively. Increasing the temperature will increase the etching rate of amorphous carbon (Table 1, 2). Increasing the thermal annealing under oxygen would create more pores covering

the whole of the carbon fibers [38]. This porous structure would increase the available surface area for electrochemical reaction, as observed in other studies relevant to thermal treatment [39].

3.3. Effect of thermal treatment time

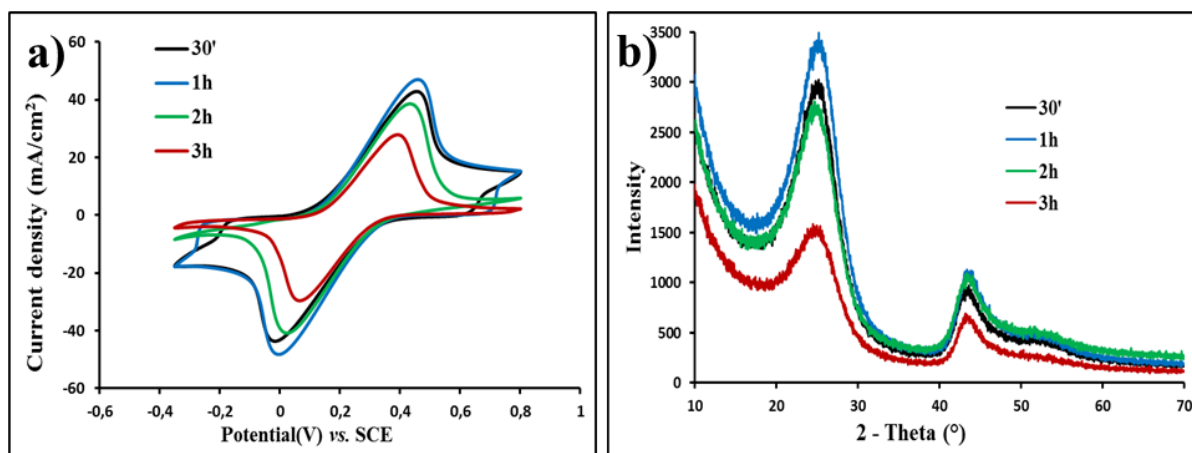


Figure 3. (a) Cyclic voltammograms (CVs) in potassium hexacyanoferrate solution at scan rate 7 mV/s, and (b) X-ray diffraction patterns of electrodes at different treatment times.

To understand deeply the effect of thermal treatment, various tests were performed under different times at a temperature of 1000°C under a nitrogen flow mixing with 1% oxygen. Peak currents observed on the cyclic voltammograms (CVs) increased with time from 30 min to 1h (Figure 3a). Nevertheless, a strong drop was noticed continuously from 2h to 3h which resulted from the destruction of carbonaceous framework due to the high reaction rate between oxygen and carbon at this temperature. In fact, by increasing the time at 1000°C, graphitic carbon is also oxidized which induces the decrease of the average crystallite size and the structural demolition. This phenomenon was often observed in studies using thermal treatment [40, 41]. It could be seen in Figure 3b, as treatment time was lengthened to 3h, the average crystallite size declined significantly (Table 2). Simultaneously, the pore system was also demolished, leading to the drop of pore volume to 0.0041 cm³/g and pore size was enlarged to 42.2 Å (Table 1). Therefore, the choice of a suitable applied treatment temperature or time was important to get both good property and conservation of initial carbonaceous structure.

3.4. Mineralization of paracetamol by electro-Fenton reaction

The prepared cathode was applied to degrade paracetamol (PCM) in acidic aqueous medium by the electro-Fenton (EF) reaction. The mineralization degree of treated solution was monitored by TOC to indicate the efficiency of EF process. As seen on the Figure 5a, the TOC removal rate after 2h treatment using PCF cathode was 31% higher than on raw CF, proving that the PCF was a promising electrode for the elimination of recalcitrant pharmaceutical pollutants using EF technology. The outstanding performance of PCF could be ascribed to the better hydrophilicity, higher electroactive surface area and crystallinity after thermal treatment. The better crystallization should also contribute to rise conductivity of PCF which encourage faster electron transport in framework for more H_2O_2 production from oxygen reduction reaction (ORR) [17]. In fact, the accumulations of H_2O_2 on PCF cathode was 24.6 mg L^{-1} , which was nearly 3 times higher than 7.9 mg L^{-1} on raw CF after 80 min (Figure 4a). Experiment degradation was controlled at a constant applied current of -40 mA (-20 mA/cm^2). The observed cell voltage was 3.9 V for PCM instead of 5.3 V for raw CF definitely because of the carbon fibres resistance decreases. It was noticed that the porous structure also helped dissolved oxygen in electrolyte solution to move easily and quickly to the whole sites of cathode. Abundant amount of hydroxyl radical ($\cdot\text{OH}$) was then generated and used here as oxidizing agent.

In contrast, in the case of bare cathode, because of hydrophobic characteristic, oxygen molecules could less easily move insight the network, so the EF reaction just happened difficultly at the cathode surface. In point of fact, raw CF was still awash while PCF was submerged immediately when contacting with electrolyte solution (Figure 4b).

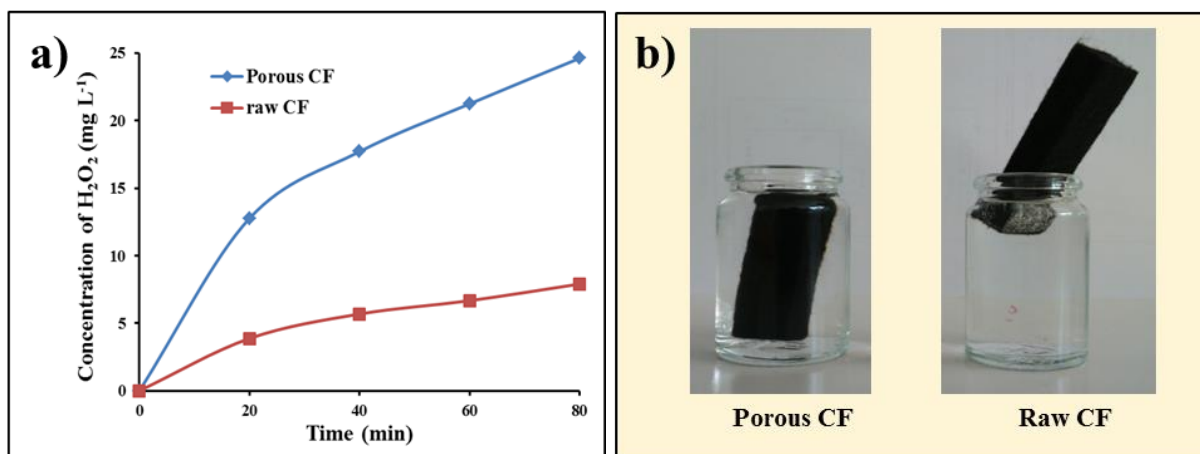


Figure 4. (a) The H₂O₂ concentration–time curves of Porous CF and raw CF at current density of -20 mA/cm², 30 mL of Na₂SO₄ 50 mM, and pH=3, and (b) Image of different cathodes in electrolyte solutions.

The degradation of PCM attained 51% in 2h treatment, and increase slowly due to the formation of the persistent complexes between iron catalyst and carboxylic acids like oxamic acid, oxalic acid coming from the bond cleavage of initial paracetamol molecule. These complexes are very difficult to mineralized by •OH, thus limiting the oxidation ability of EF, as noticed by E. Brillas *et al.* [42]. The mineralization of PCM was considered as finished after 10h when TOC removal reaches 94 % (Figure 5a). The stability of modified cathode was monitored by cleaning PCF electrode with deionized water and reusing for degradation of PCM under the same conditions. The mineralization ratio on recycling cathode showed a little change after 10 cycles. This very small decrease observed in Figure 5b could be attributed to the mislaying of carbon fibers during the washing process. This stable performance proved that PCF is a promising cathode which could be applied in environmental fields to treat wastewater polluted containing Persistent Organic Pollutants (POPs) by EF technology.

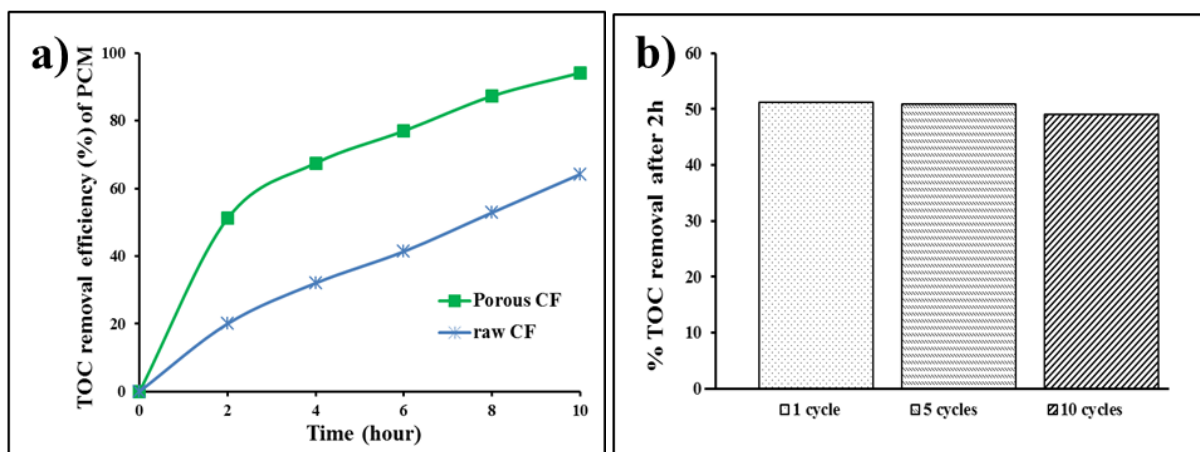


Figure 5. (a) TOC removal efficiency (%) of PCM on Porous CF and raw CF during 10 h. (b) TOC of PCM removal after 2 h treatment on PCF during 10 cycles. Conditions: Pt anode; V=30 mL, [PCM]=0.1 mM; [Fe²⁺]=0.2 mM; pH=3; [Na₂SO₄]=50 mM, and I = -20 mA/cm².

4. Conclusion

By using the thermal treatment of carbon felt under gas flow containing 1% of oxygen in tubular furnace during 1h at 1000°C, a porous carbonaceous material was fabricated due to the selective etching of amorphous carbon. Porous carbon felt (PCF) electrode presented such outstanding properties compared to non-modified one (raw CF) like: a surface area 700 times higher, a better hydrophilicity, a higher developed crystallization and an expanded electroactive surface area. The new material proved its significant efficiency once it was applied as cathode in EF process to remove PCM in acidic aqueous medium. The TOC removal was 51% in 2h treatment which was 31% higher than on raw CF. The value reached 94% after 10h treatment which was a particularly interesting result for a refractory molecule like PCM. Relying on the excellent electrochemical characteristic as well as the stability after 10 cycles, PCF was expected to be used in other promising fields like biofuel cells.

5. Acknowledgments.

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