Heterogeneous electro-Fenton using a Printex L6 carbon-based cathode modified with ferrocene for degradation of paracetamol at neutral medium

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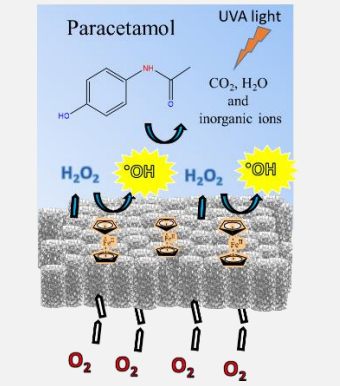

This study investigated the use of ferrocene (Fc), a low-cost and environmentally friendly compound, to enhance a carbon-based gas diffusion electrode (GDE) for heterogeneous electro-Fenton treatment of paracetamol-containing solutions under neutral pH conditions. Under optimized conditions, the contaminated water was exposed to UV-A light, revealing a synergistic effect, especially with Fc-modified GDEs. Negligible iron (Fe) leaching, with a mere 0.06 mg L^{-1} detected in the 5% Fc-modified GDE case was observed, which is a remarkable outcome. Therefore, these cathodes represent a very convenient option for the photoelectrocatalytic degradation system and have become a promising choice for highly efficient and environmentally friendly water decontamination processes.

Introduction

In recent years, much attention has been paid to the potential adverse effects of pharmaceutical contaminants in aquatic ecosystems and human health. The water pollution by pharmaceutical compounds is a result of the poor efficiency of conventional processes used for the treatment of effluents generated by the pharmaceutical industry and hospitals, and the improper disposal of unused pharmaceuticals reaching sewage system [1-2]. Particularly, paracetamol (PCT) is one of the most used pharmaceuticals worldwide as antipyretic and analgesic. Due to this, PCT and its metabolites has been frequently detected in surface water, wastewater and drinking water [1].

The use of electrochemical advanced oxidation processes (EAOP) has been proposed as an alternative oxidation technology for the removal of pharmaceuticals [4]. In the present study, heterogeneous Electro-Fenton using a ferrocene modified gas diffusion electrode was employed to treat paracetamol aqueous solution.

To date, none of studies employed Fc as supported heterogeneous catalyst in carbonaceous matrix to for dual role: i.e. electrogeneration of H_2O_2 and its activation. Taking into account the characteristics of Fc, in this study we propose a novel gas diffusion electrode based on Printex carbon L6 modified with Fc to treat paracetamol aqueous solutions.

Material and Methods

To fabricate the unmodified GDE and Fc modified-GDE (Fc-GDE), a catalytic mass composed of PL6C (w/w 80%) and PTFE (w/w 20%) is spread over a commercial carbon cloth as previously described by [16]. The H_2O_2 electrogeneration and paracetamol (PCT) degradation tests were conducted in a batch electrochemical reactor equipped with a platinized Ti anode and GDEs prepared as cathodes (Fig 1). For H_2O_2 electrogeneration, the electrolyte was composed of 0.2 L of 0.1 mol L^{-1} K_2SO_4 solution, while the O_2 flow rate (0.05 L min^{-1}) through GDE. The electric current applied was 0.15, 0.3, and 0.5 A. Then, irradiation of systems (using unmodified GDE, 5% Fc-GDE, and 15% Fc-GDE) with UV-A light was conducted at 7.5 mA cm^{-2} leading to the photoassisted heterogeneous electro-Fenton.

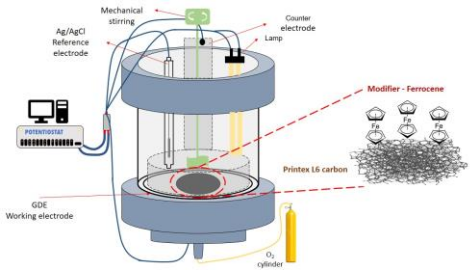

Figure. 1. Schematic diagram of the three-electrode cell used to evaluate the three different prepared GDEs for electrosynthesis of H_2O_2 and degradation of PCT.

Results and Discussion

The impact of current density on the degradation of PCT was evaluated at three different current densities (7.5, 15, and 25 mA cm^{-2}) using unmodified GDE, 5% Fc-GDE, and 15% Fc-GDE. Figure 1 indicates that an increase in current density did not result in a higher rate of PCT degradation for 5% Fc-GDE, and this behaviour was observed for all GDEs studied. This was determined by analyzing the charge applied per electrolyzed volume.

This phenomenon may be attributed to parallel reactions (Eqs. 1-3) that are promoted at elevated current densities, which inhibit the main heterogeneous reaction (Eq. 4).

$$^{\bullet}OH \rightarrow O_2 + 2H^+ + 2e^- \quad (1)$$

$$2\ ^{\bullet}OH \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

$$Fc+ + H2O \rightarrow Fc + \bullet OH \quad (4)$$

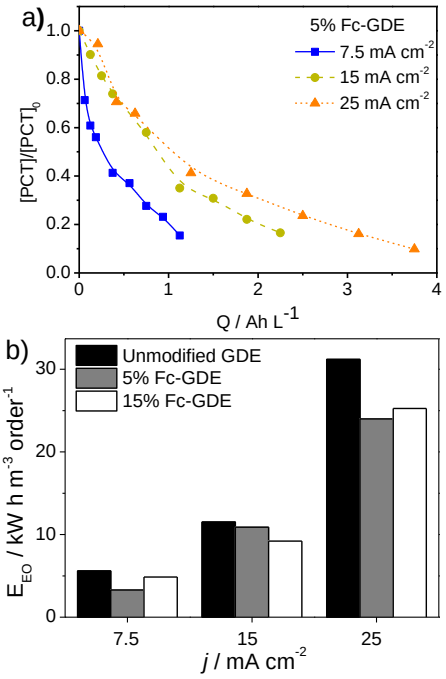

Figure 2. PCT removal as a function of applied electric charge per unit volume for the 5% Fc-GDE (a) and (b) energy consumption per order of contaminant removed. Conditions: [PCT_0] = 10 mg L^{-}, t = 90 min, pH = 7.

Under O_2 flow a UV-A irradiation, with generation of H_2O_2 by electrolysis, the degradation rate of PCT is significantly enhanced, which can be attributed to the presence of H_2O_2 which accelerates the degradation by forming $^{\bullet}OH$ species. Also, the removal of TOC increased with the use of Fc-GDE. In terms of energy consumption, again the system using 5% Fc-GDE proved to be the most energy efficient, as shown in Fig. 3.

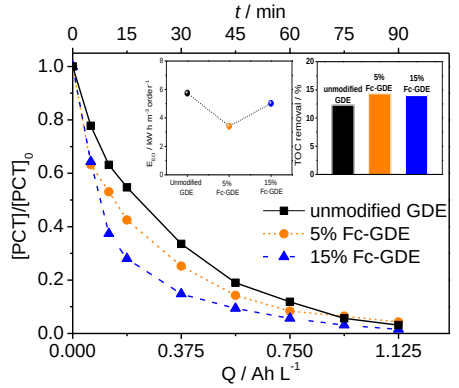

Figure 3. PCT degradation curves of unmodified GDE and Fc-GDEs under UV-A irradiation under OE/H_2O_2/UV-A process. Inset: energy consumption per order of contaminant remove in kWh m^{-3} $order^{-1}$ and TOC removed.

Finally, the results have shown that the 5% Fc-GDE (Figure 4) is the optimal choice among the GDEs tested regarding lower current densities and energy consumption.

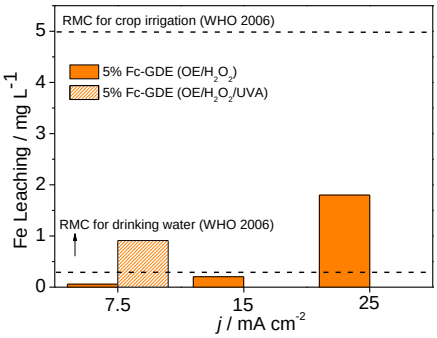

Figure 4. Iron leaching after PCT degradation using 5% Fc-GDE under different conditions. Conditions: [PCT_0] = 10 mg L–1, pH = 7, t = 90 min, 0.1 mol L^{-1} K2SO4, UV-A = 9 W.

Conclusions

A novel Fc-modified GDE was successfully developed to effectively treat PCT-contaminated water. PCT degradation has better performance at lower current density and lower energy consumption using the modified electrode with 5% Fc. The degradation efficiency presented a significant enhancement under UV-A irradiation, especially for 15% Fc-MGDE, which can be explained by the interaction of Fc with UV-A light to form additional •OH species; however, analyzing results in terms of energy consumption and TOC removal, the 5% Fc-GDE appears as a most appropriate cathode. Iron leaching was minimal during the process demonstrating that this electrode can efficiently be used for the degradation of PCT from neutral water matrices and ensure the safety of water to be reused, for example, for crop irrigation.

Acknowledgments

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