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Effect of air pressure on the electro-generation of H_2O_2 and the abatement of organic pollutants in water by electro-Fenton process

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ABSTRACT

The electro-generation of H_2O_2 and the abatement of the model organic pollutant Acid Orange 7 (AO7) in water by an electro-Fenton process were performed under moderate air pressures (up to 11 bar) for the first time to our knowledge. An increase of the pressure gave rise to a drastic enhancement of the concentration of hydrogen peroxide. In systems pressurized with air at 11 bar, the electro reduction of oxygen at a graphite cathode gave rise to a concentration of H_2O_2 of about 12 mM, about one order of magnitude higher than that achieved at atmospheric pressure. This result is attributed to the mass transfer intensification induced by the higher local concentration of molecular oxygen dissolved in the aqueous phase. Similarly, for electro-Fenton, a drastic increase of the TOC abatement was achieved upon increasing the air pressure. The effect of the current was also investigated in detail.

1. Introduction

The environmental protection requires advanced processes for the treatment of wastewater contaminated by organic pollutants which are resistant to conventional biological processes. Within this context, great progress has been made in the electrochemical technologies. The main electrochemical procedures utilized for the remediation of wastewater are electroreduction, electrochemical oxidation and indirect electro-oxidation with active oxidants [1]. The most important advantages of electrochemical methods for the treatment of wastewater are their high efficacy, mild operation conditions, ease of automation, versatility and low costs, especially when they are powered by renewable energy from wind and solar sources [1–4]. Recently, the treatment by emerging technologies such as electro-Fenton (EF) has received a great deal of attention [4]. EF process is a very promising tool for the treatment of wastewater contaminated by a wide series of organic pollutants resistant to conventional biological processes [4]. It is based on the electro-generation of hydrogen peroxide in aqueous solution by two-electron reduction of dissolved oxygen (eq. (1)), directly injected as pure gas or bubbled air, on a cathode such as mercury pool [5] or carbonaceous materials, such as compact graphite [4,6–7], carbon felt [4,8–9], reticulated vitreous carbon [4,10] and carbon-polytetrafluoroethylene (carbon-PTFE) gas diffusion electrodes (GDE) [4,11]. The utilization of air is usually preferred for its low cost with respect to oxygen. The oxidizing power of H_2O_2 is enhanced in the presence of Fe^{2+} via classical Fenton's reaction (Eq. (2)) which leads to the production of hydroxyl radicals.

$$O_2 + 2H^+ + 2\ e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\bullet + OH^- \quad (2)$$

Reaction (2) is propagated through the continuous electro-generation of Fe^{2+} by cathodic reduction of Fe^{3+} (Eq. (3)).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

H_2O_2 is consumed by cathodic reduction (Eq. (4)), disproportionation (Eq. (5)) and in undivided cells, often used to avoid the voltage penalty of the separator, anodic oxidation (Eq. (6)) [4,11].

$$H_2O_2 + 2H^+ + 2\ e^- \rightarrow 2\ H_2O \quad (4)$$

$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O \quad (5)$$

$$H_2O_2 \rightarrow O_2 + 2\ H^+ + 2e^- \quad (6)$$

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Consequently, the rate of H_2O_2 accumulation is lower than its rate of electro-generation. Due to the poor solubility of O_2 in aqueous solutions at 1 atm and 25 °C (about 40 or 8 mg L^{-1} in contact with pure oxygen or air, respectively) [12] two dimensional cheap graphite electrodes give quite slow generation of H_2O_2, thus resulting in low H_2O_2 bulk concentrations especially in undivided cells [4,7]. The generation of H_2O_2 is usually accompanied by the parasitic cathodic evolution of hydrogen (eq. (7)) while at the anode the oxygen evolution reaction is expected (Eq. (8)).

$$2H^+ + 2\ e^- \rightarrow H_2 \quad (7)$$

$$2\ H_2O \rightarrow O_2 + 2\ H^+ + 2\ e^- \quad (8)$$

Various approaches have been described in the literature to increase the local concentration of H_2O_2 [4,7,13–15,27]. Concentrations of H_2O_2 higher than 50 mM in divided cells separated by cationic membranes [4,13] were reached by injecting the gas through GDEs which have higher costs and require a more complicated electrochemical cell layout. An increase of the concentration of H_2O_2 of about one order of magnitude was obtained using microfluidic electrochemical devices equipped with cheap compact graphite cathodes at proper operating conditions [7,14]. A significant increase of the concentration of H_2O_2 was also obtained using dual rotating graphite felt disks [15].

A high concentration of hydrogen peroxide could be theoretically also obtained by increasing the solubility of oxygen in water by using pressurized air or oxygen, thus potentially improving the performances of the EF process. In this context, we report here, for the first time to the best of our knowledge, a study on the effect of the air pressure on both the electro-generation of hydrogen peroxide and the abatement of organic pollutants in water by an electro-Fenton process. Moderate air pressures (1–11 bar) easily achievable in applicative scale electrochemical reactors were used. An increase of the concentration of H_2O_2 of about one order of magnitude was obtained by working at proper operating conditions with moderate air pressure (up to 11 bar). Similarly, a drastically higher abatement of the Acid Orange 7 (AO7), an azoic dye selected as a model organic pollutant resistant to conventional biological processes, was obtained by performing the electro-Fenton process upon increasing the air pressures.

Due to their large-scale production and extensive application, synthetic dyes can cause considerable non-aesthetic pollution and are serious health-risk factors [17]. Since dyes usually present high stability under sunlight and resistance to microbial attack and thermal degradation, most of these compounds are not degradable in conventional wastewater treatment plants. Electrochemical methods are considered to be among the more efficient Advanced Oxidation Processes (AOPs) for the removal of dyes [17]. The azo dye Acid Orange 7 (AO7), also called Orange II ($C_{16}H_{11}N_2NaO_4S$), was often chosen as model compound to evaluate promising abatement approaches because, as a simple molecule, it can easily be used to test new methodologies; in addition, it is widely used for coloration in paperboard industries and in wool textile dyeing.

The electrochemical oxidation of aqueous solutions of AO7 was previously investigated by various authors [18–26]. The anodic

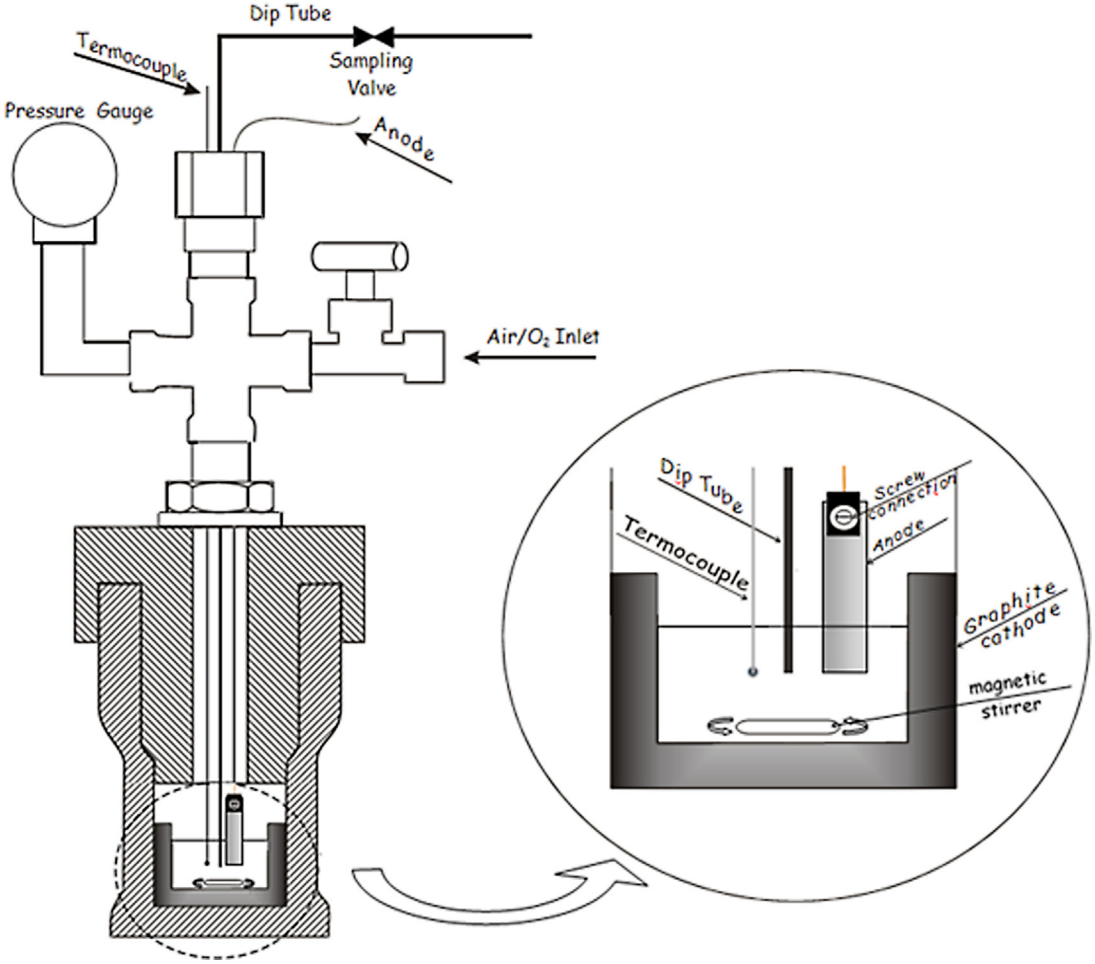

Fig. 1. Schematic diagram of the experimental cell.