



A complete phenol oxidation pathway obtained during electro-Fenton treatment and validated by a kinetic model study



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ARTICLE INFO

Article history:

Received 19 March 2015

Received in revised form 4 June 2015

Accepted 11 June 2015

Available online 19 June 2015

Keywords:

Aromatic compounds

Electrochemical advanced oxidation processes

Hydroxyl radical

Mathematical modelling

Oxidation by-products

Sensitivity analysis

ABSTRACT

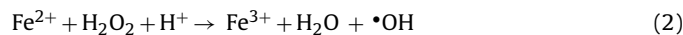
A new approach of electro-Fenton modelling is proposed with phenol (PH) as a target contaminant. Five representative steps involved in the process have been considered: (i) H_2O_2 *in situ* generation, (ii) Fenton's reaction in bulk solution, (iii) Fe^{2+} (catalyst) electroregeneration, (iv) scavenging reactions (v) oxidative degradation and mineralization of PH as target pollutant. A new complete mineralization pathway of PH is proposed by gathering many intermediates that were found in different papers in literature and by adding some other ones to complete the oxidation route. A total number of 27 oxidation by-products of PH are considered, which represents 28 differential equations including PH. A sensitivity analysis of second-order kinetic parameters has been performed. It confirms the usefulness of the 49 kinetic reactions that have been taken into account and the importance of the five steps of the process, especially the fourth one. Based on existing parameter values found in literature, kinetic parameter estimations have been performed in order to better fit the experimental results. The model efficiency (ME), the root mean square error (RMSE) and the index of agreement (IoA) calculated to evaluate the performance of the model compared with experimental data have shown respectable values, which validate the model and the pathway. This model represents new understandings in mechanisms that occur during electrochemical advanced oxidation processes. It also improves the prediction of the concentration profiles of aromatic organic compounds and their intermediates.

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1. Introduction

Hazardous and harmful compounds like phenol (PH) and its well-known by-products like hydroquinone (HQ) and para-benzoquinone (pBQ) are often found in wastewater mainly from petrochemicals industries, paint, pesticide, coal conversion [1]. Solutions containing many xenobiotics and especially aromatic compounds may undermine a biological process. Advanced oxidation processes (AOPs) have been developed as alternative technologies to conventional processes in recent decades [2,3] for treating recalcitrant pollutants. AOPs produce *in situ* hydroxyl radical ($\bullet OH$), the strongest oxidizing agent ($E^\circ = 2.80 V/SHE$, [4]) after fluorine. The latter is to be avoided because of its aggressivity in aqueous medium. These processes are especially efficient for aromatic molecules thanks to their non-selective electrophilic aro-

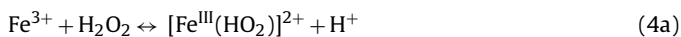
matic substitution of hydroxyl radical to aromatic moieties, leading finally to the ring opening reactions. Among AOPs, the emerging electro-Fenton process has shown promising results especially for industrial wastewaters treatment [5,6]. In contrast to the classical Fenton process, H_2O_2 is generated *in situ* at the cathode with O_2 or air feeding (Eqs. (1a)–(1d)) while an iron catalyst (Fe^{2+} , Fe^{3+} , or iron oxides) is added to the effluent to produce $\bullet OH$ at the bulk acidic solution *via* Fenton's reaction (Eq. (2)) [5,7]:



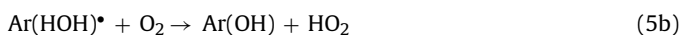
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Fe²⁺ can then be electrocatalytically *in situ* regenerated mainly through Eq. (3) and secondly through Eqs. (4a)–(4c):



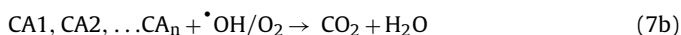
The aromatic compounds (ArH) can then be hydroxylated (Ar(OH)) through Eqs. (5a) and (5b):



The hydroxylated compounds can then be oxidized in carboxylic acids (CA) following ring opening reactions through the following equation:



Carboxylic acids thus formed can then be degraded in lower molecular weight CAs and finally mineralized to CO₂ as ultimate mineralization product:



The electro-Fenton process is considered as a clean treatment by minimizing the use of reagent and avoiding parasitic reactions without any production of sludge. Furthermore, the rate of organic pollutant removal as well as the mineralization yield are usually significantly higher than for classical chemical Fenton treatment [5].

Most of the kinetic models on AOPs have been proposed with UV/H₂O₂ treatment [8], classical Fenton process [9–16], Fenton-like treatment [17–19] and photo-Fenton process [20–22]. However, only two papers refer to electro-Fenton process [23,24]. Liu et al. [23] performed electro-Fenton in batch experiments and considered seven standard equations to model the evolution of H₂O₂ and the PH degradation by varying the concentration of initial Fe²⁺, the oxygen concentration and the current density. Regalado-Mendez et al. [24] worked in continuously stirred tank reactor (CSTR) by using the same reactions as Liu et al. [23] for the model. Both studies simplified the model by not considering the oxidation by-products formed during the electrolysis, but only predict the PH concentration decrease.

However the prediction of the evolution of intermediates is also required since their toxicity can sometimes be even higher than the toxicity of the initial pollutant [25,26]. In the present study a new complete mineralization pathway of a representative pollutant such as PH treated by electro-Fenton is presented. This pathway describes the evolution of concentrations of intermediates like HQ, pBQ, catechol (CT), resorcinol (RS), maleic acid (MLE), fumaric acid (FUM), succinic acid (SUC), glyoxylic acid (GLYOX), oxalic acid (OXA) and formic acid (FOR). Sensitivity analysis and model validation by comparing model simulations with experimental data are then performed.

2. Modelling

2.1. Steps involved in the electro-Fenton process

Fig. 1 highlights the 5 main groups of reactions involved in the electro-Fenton process, namely (i) H₂O₂ *in situ* generation, (ii) Fenton reaction in bulk solution, (iii) Fe²⁺ (catalyst) electroregeneration, (iv) scavenging reactions (v) oxidative degradation and

mineralization of PH and its degradation. The developed model follows these 5 steps.

2.2. Assumptions

The assumptions made to establish the model are listed below:

- The adsorption of compounds and especially PH on carbon-felt cathode during the electro-Fenton treatment is considered negligible (less than 1% of adsorbed PH),
- The interferences from sulphate ion (SO₄²⁻) and derivative species that could come from the electrolyte are considered negligible. The hydroperoxo iron complexes that could be formed [17] would not reduce the availability of iron since they can regenerate Fe²⁺ from Eqs. (4a)–(4c) [5],
- All the reactions were considered irreversible except the reactions between HQ and pBQ, between CT and oBQ and between MLE and FUM [27,28],
- No precipitation of iron(III) during experiment (low iron ion concentration and acidic medium) and the concentration of Fe²⁺ during the electrolysis was considered to be proportional to its initial concentration [23],
- The dissolved oxygen concentration ([O₂]_{dissolved}) is at saturation in the solution before starting the experiment and during the experiment, which permits to assume that [O₂]_{dissolved} is constant during all the experiments [23],
- The concentration of H⁺ and OH⁻ were considered constants, since the pH of the reaction medium remains constant during the experiments,
- The concentration of Fe²⁺ during the treatment was considered to be constant [23],
- The volume of reaction and the temperature of solutions were considered constant,
- The quasi-steady state approximation (QSSA) hypothesis was considered for hydroxyl radicals because they have very short half-time and are continuously produced and destroyed at a similar rate to attain a steady-state concentration in the bulk and/or the vicinity of the anode [5],
- The solutions are considered to be perfectly mixed and concentrations of compounds depend only on the treatment time,
- Polymerization, condensation, dimerization reactions were assumed to be negligible compared to the whole process of degradation by electro-Fenton [27].

2.3. Mass-balance equations

In batch experiments, the mass-balance equations can be determined according to the following equation:

$$\frac{dC_i}{dt} = R_i = \sum_n v_{i,n} r_n \quad (8)$$

where C_i is the molar concentration of compound i, v_{i,n} is stoichiometric coefficient of compound i in reaction n, r_n is the reaction rate of reaction n and R_i is the production/consumption rate of compound i.

The chemical reactions selected to determine the pathway of PH during electro-Fenton treatment are represented in Table 1. There are 49 Reactions with 52 kinetic constants considered.

The matrix of equations used to elaborate the model is mentioned in Table SI-1 in supporting information. There are 30 differential equations and 1 algebraic equation that come from the QSSA of hydroxyl radical compound (Text SI-1 in supporting information). It represents 32 compounds that are considered including 4 inorganic compounds (H₂O₂, CO₂, Fe²⁺ and •OH) and 28 organic compounds (PH and its oxidation by-products).

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