ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Kinetic modeling of CWPO wastewater treatment over 3D-printing Fe/SiC monolith catalysts

Asunción Quintanilla*[1], Pilar Miranzo[2], M. Isabel Osendi[2], Manuel Belmonte[2], Jose A. Casas[1]

1 Chemical Engineering Section, Universidad Autonoma de Madrid, 28049 Madrid, Spain; 2 Institute of Ceramics and Glass (ICV-CSIC), 28049 Madrid, Spain

**Corresponding author: asun.quintanilla@uam.es*

Highlights

- Robust 3D printed Fe/SiC monoliths were fabricated by direct ink writing.
- Fe/SiC monoliths exhibit good catalytic activity and long-term stability for CWPO.
- Diffusion of phenol through the cell wall controlled the overall reaction rate.
- A power-law kinetic model for phenol and TOC removal and H_2O_2 consumption is presented.

1. Introduction

The recent fabrication of robust three-dimensional (3D) Fe/SiC monolithic catalysts by robocasting, a filament-based printing method, has opened new perspectives in the reactor engineering solution for industrial wastewater treatments through the design and direct printing of structured reactors [1]. Catalytic wet peroxide oxidation (CWPO) process is one of the most promising technologies to remove pollutants organics from non-biodegradable contaminated waters by oxidation with H_2O_2 under mild conditions (temperature and pressur in the range of 25-100 ºC and 0.1-0.5 MPa, respectively) [2].

Herein, we offer a better insight into the CWPO processes with 3D-printing Fe/SiC monolith catalysts by the development and validation of a kinetic model to describe the space time dependence of the pollutant disappearance (phenol), total organic carbon removal and H_2O_2 consumption. This study will helpful for designing large-scale CWPO reactors and optimizing their operative performance.

2. Methods

Printable Fe-doped SiC inks were prepared by planetary centrifugal mixing the corresponding amounts of β-SiC nanoparticles (d=45-55 nm and [Fe]=0.52 wt.%), polymeric binders (polyethyleneimine and methylcelulose) and deionized water. 3D cylindrical periodic lattices (d_m=12 mm, h_m=4.5 mm, d_{ch}= 1.2 mm, δ_w= 270 µm, 74 cells/cm^2) were computer designed and printed at room temperature onto an alumina substrate with a custom three-axis robocasting system using tips with inner diameter of 330 µm. Then, the monoliths were treated at 600 ºC for 2 h in air to burn-out the organics and, afterwards, Spark Plasma Sintered (SPS) in argon atmosphere at 1200 ºC. Oxidation experiments were carried out in a quartz up-flow reactor (d_i=15 mm) loaded with nine Fe-doped SiC cylindrical monoliths (W=2.83 g, V_R=4.5 cm^3 and ε_m=0.67) in isothermal conditions. Phenol was selected as target pollutant. The reactor was operated at a temperature and space time (τ) range of 65-85 ºC and 0-378 g_{CAT}·h/L, respectively. The concentration of phenol in distilled water was varied between 0.5-1.5 g/L and H_2O_2 between 2.5-6.5 g/L.

3. Results and discussion

Complete phenol disappearance, 70% TOC removal and 75% H_2O_2 consumption were achieved at 85 ºC and 378 g_{CAT}·h/L (equivalent to a tr=36 min), using the stoichiometric dose of H_2O_2 for the oxidation of 1 g/L of phenol. These results demonstrate the good catalytic activity exhibited by the Fe/SiC monoliths. Also, the monolithic catalyst was stable in long-term experiments (400 h).

External mass-transfer resistance, experimentally studied by using two monolith reactors loaded with different mass of catalyst (W=2.8 and 0.97 g_{cat}), did not affect the reaction rate since the same conversion profiles *vs.* WHSV were obtained. In contrast, internal mass transfer limitation could not be excluded. The

internal effectiveness factor, calculated from the Thiele Modulus assuming a pseudo first-order reaction with a characteristic length value equal to half of the δ_w varied from 0.94 (at 65 ºC) to 0.85 (at 85 ºC).

The kinetic modeling of the CWPO of phenol with 3D printing Fe/SiC monoliths was discriminated by fitting potential and LHHW-type equations to the experimental phenol, TOC and H_2O_2 concentration profiles obtained under the different operating conditions studied for space-time from 0 to 378 g_{CAT}·h/L. The set of potential expressions for the intrinsic kinetics that minimized the sum of squared residuals and the objective function used by OriginPro 8 are the following:

$$(-r_{fenol})\left(\frac{mol}{g_{cat}\cdot h}\right) = 1.1\cdot 10^{5}\cdot e^{-\frac{5617\pm 39}{T}}\cdot C_{fenol} \quad [1]$$

$$(-r_{TOC})\left(\frac{mol}{g_{cat}\cdot h}\right) = 1.2\cdot 10^{12}\cdot e^{-\frac{10662\pm 1806}{T}}\cdot C_{TOC}^{2} \quad [2]$$

$$(-r_{H2O2})\left(\frac{mol}{g_{cat}\cdot h}\right) = 2.0\cdot 10^{6}\cdot e^{-\frac{7055\pm 2578}{T}}\cdot C_{H2O2} \quad [3]$$

Noteworthy, phenol disappearance and TOC removal are not affected by the oxidant concentration, unless in the range from 100 to 130% of the stoichiometric dosage here employed, which is an interesting result regarding to the cost-effectiveness of the H_2O_2-promoted oxidation processes, like CWPO. The activation energy values of 47, 89 and 59 kJ/mol for phenol, TOC and H_2O_2, respectively, show the strong influence of the temperature, in particular in the mineralization reaction. The validation of this model is illustrated by the parity plots in Figure 1.

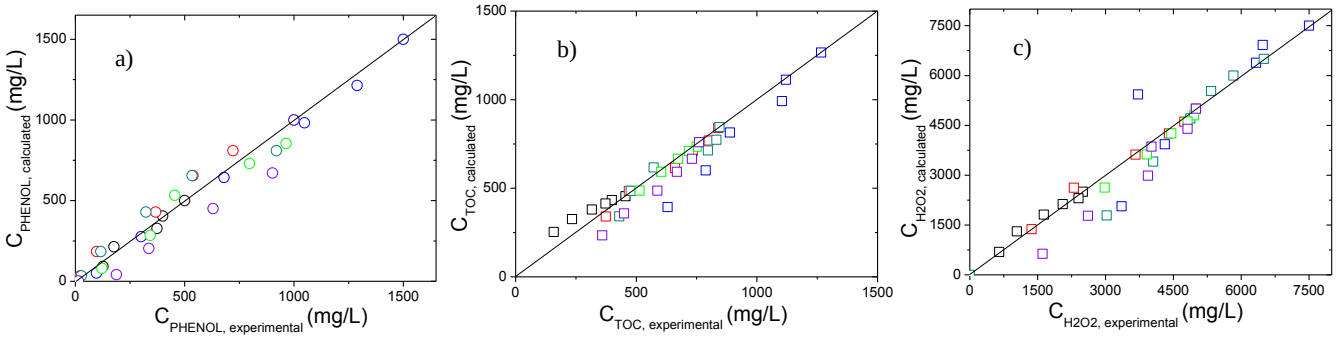

Figure 1. Parity plot of measured and simulated values from [Eq. 1-3] for phenol (a), TOC (b) and H_2O_2 (c) concentration (mg/L) under the different operation conditions tested in this work.

4. Conclusions

A novel insight into the CWPO performance in monolith reactor has been presented. The application of these reactors has been demonstrated by the modeling of phenol oxidation and mineralization and H_2O_2 consumption considering the internal diffusion control and assuming plug-flow in each channel. The discriminated kinetic model successfully agreed with the experimental data under different experimental conditions. The results showed that dosage of H_2O_2 above the stoichiometric amount did not impact the efficiency of the wastewater oxidation treatment.

References

[1] A. Quintanilla et al. EAAOP5 Conference, June 25-29, 2017, Prague, Czech Republic.
[2] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, Catal. Today, 55 (2000) 61-69.

Keywords
3D-printing; monolith reactor; catalytic wet peroxide oxidation; kinetic model