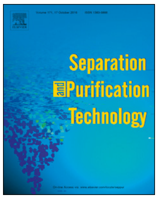
Separation and Purification Technology 209 (2019) 301–306

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Intensification of catalytic wet peroxide oxidation with microwave radiation: Activity and stability of carbon materials

Alicia L. Garcia-Costa*, Juan A. Zazo, Juan J. Rodriguez, Jose A. Casas

Chemical Engineering Departamental Section, School of Science, Universidad Autonoma de Madrid, Ctra. Colmenar Viejo km. 15, Madrid 28049, Spain

ARTICLE INFO

Keywords:
CWPO
Microwave
Activated carbon
Graphite
Hot spot

ABSTRACT

Several commercial carbon materials have been tested as catalysts in the Microwave-assisted Catalytic Wet Peroxide Oxidation process (MW-CWPO). Two graphites (G-F and G-S), two activated carbons (AC-M and AC-C), two carbon blacks (CB-V and CB-A) and silicon carbide (SiC) were selected due to their MW-absorbing properties. Phenol (100 mg L^{-1}) was used as target pollutant, operating in batch at pH_0 3, 120 °C, 500 mg L^{-1} catalyst load and the theoretical stoichiometric amount of H_2O_2 (500 mg L^{-1}). All carbon materials showed to be active in terms of H_2O_2 decomposition and phenol oxidation. Nonetheless, G-S and AC-M stood out as the most active materials in terms of TOC removal, with values of 94 and 93% TOC elimination, respectively. On the other hand, both carbon blacks and G-F yielded a significantly lower TOC degradation. Surface chemistry seems to rule the activity of graphites, in particular the pH slurry (4.5 for G-S and 8.4 for G-F). The most active catalysts, G-S and AC-M were used in 5 consecutive cycles in order to study their stability. While G-S remained active, AC-M.

1. Introduction

Public and governmental concern on water quality challenges engineers to find new or enhanced technologies for wastewater treatment, particularly when facing bio-refractory pollutants. Catalytic Wet Peroxidation (CWPO) appears to be a potential solution. This Advanced Oxidation Process (AOP) consists a heterogeneous version of the Fenton process, based on the redox decomposition of H_2O_2 into hydroxyl ($HO^{\cdot}$) and hydroperoxyl radicals ($HOO^{\cdot}$). These species present high oxidation potentials, high reactivity and low selectivity, allowing the breakdown of organic recalcitrant pollutants. Furthermore, this is an environmentally friendly technology, since H_2O_2 decomposition yields non-toxic byproducts. CWPO catalysts frequently consist on a metallic phase (Fe, Cu) supported on activated carbon, alumina or other porous materials [1–5]. Nonetheless, catalyst deactivation due to metal leaching is usual, generating a new environmental problem. To overcome this issue, several authors have successfully employed bare carbon materials such as activated carbon, graphite or carbon black as CWPO catalysts [6–10].

CWPO intensification has been studied in the past decades, addressed to improve both the overall efficiency of the process and the catalyst stability [11]. In this sense, several strategies have been checked, like working at higher temperature [10,12], or applying different radiations, such as UV–vis [13,14], ultrasounds [15] and microwaves (MW) [16–22]. Within these new processes, microwave-assisted CWPO (MW-CWPO) offers a promising way allowing to work at higher temperature with a more efficient heating. Besides, when using MW absorbers, such as carbon materials, hot spot formation on their surface can occur. Delocalized π-electrons in the surface of carbon materials are free to move. The kinetic energy of these electrons increases upon MW irradiation, generating micro-plasmas, or hot spots, and ionizing the surrounding atmosphere These hot spots may reach up to 1200 °C and have a synergistic effect on CWPO, boosting $HO_x^{\cdot}$ generation [22–25].

Table 1 summarizes the most recent applications of MW-CWPO for wastewater treatment. Research efforts are being addressed on the development of complex nanocomposites and their applications in MW-CWPO, with some outstanding results [26–29]. Nonetheless, a better knowledge is needed on key issues such as H_2O_2 decomposition, pollutants mineralization, degradation pathways and catalysts stability. Furthermore, even the reported operating conditions need to be clarified in some cases. Thus, additional systematic research is required to better understand the MW-CWPO process.

Previous work has shown that bare activated carbon (AC) yielded practically the same activity than Fe/AC catalysts (Fe: 4 wt% as Fe_2O_3) in MW-CWPO process, due to its MW absorbing properties, [30]. Hence, the use of carbon materials can offer a low-cost and feasible alternative to tailor-made traditional CWPO catalysts.

---

[*] Corresponding author.
E-mail address: alicial.garcia@uam.es (A.L. Garcia-Costa).

https://doi.org/10.1016/j.seppur.2018.07.054
Received 23 April 2018; Received in revised form 19 July 2018; Accepted 20 July 2018

Table 1
Recent works on MW-CWPO.

Pollutant	Catalyst	Operating conditions	Results	Ref.
Methyl orange (MO)	$NiFeMnO_4$	C_{MO}: 30 mg L^{-1} C_{cat}: 1 g L^{-1} C_{H2O2}: 30 mg L^{-1} t: 60 min pH_0: 2–3 T: 50 °C P: 750 W	X_{MO}: 97%	[26]
Orange G (OG)	$rGO\text{-}TiO_2$	C_{MO}: 4.5 mg L^{-1} C_{cat}, C_{H2O2}, t and pH_0: unknown T: 30–120 °C P: 300 W	X_{OG}: 90%	[27]
Perfluorooctanoic acid (PFOA)	$Pb\text{-}BiFeO_3$/rGO	C_{PFOA}: 50 mg L^{-1} C_{cat}: 1 g L^{-1} C_{H2O2}: 44 mg L^{-1} t: 5 min pH_0: 5 T: unknown P: 500 W	X_{PFOA}: 87% X_{TOC}: 52%	[28]
Phenol	CuO_X/GAC	C_{Phenol}: 100 mg L^{-1} C_{cat}: 3 g L^{-1} C_{H2O2}: 600 mg L^{-1} t: 5 min pH_0: 4 T: unknown P: 400 W	X_{Phenol}: 100% X_{COD}: 90%	[29]
Phenol	Fe/AC	C_{Phenol}: 100 mg L^{-1} C_{cat}: 0.1 g L^{-1} C_{H2O2}: 500 mg L^{-1} t: 60 min pH_0: 3 T: 120 °C P: variable P_{MAX}: 1800 W	X_{Phenol}: 100% X_{H2O2}: 100% X_{TOC}: 87%	[30]
Phenol	AC	C_{Phenol}: 100 mg L^{-1} C_{cat}: 0.1 g L^{-1} C_{H2O2}: 500 mg L^{-1} t: 60 min pH_0: 3 T: 120 °C P: variable P_{MAX}: 1800 W	X_{Phenol}: 100% X_{H2O2}:100% X_{TOC}: 80%	[30]

Table 2
Porous texture and pH slurry of the carbon materials.

Material	S_{BET} ($m^2 g^{-1}$)	A_{ext} ($m^2 g^{-1}$)	pH slurry
G-F	7	7	8.4
G-S	12	12	4.5
CB-A	74	74	6.7
CB-V	238	152	6.6
AC-C	872	73	6.8
AC-M	991	169	6.5
SiC	< 2	< 2	7

Phenol is one of the most characteristic pollutants in industrial wastewater and its degradation has been widely studied [29–32]. Therefore, it represents an interesting pollutant when comparing the performance of different catalysts in new processes, such as MW-CWPO. In this work, the activity of activated carbon, graphite, carbon black and silicon carbide as MW-CWPO catalysts for phenol oxidation has been tested. The stability of the most active materials upon consecutive runs has also been checked.

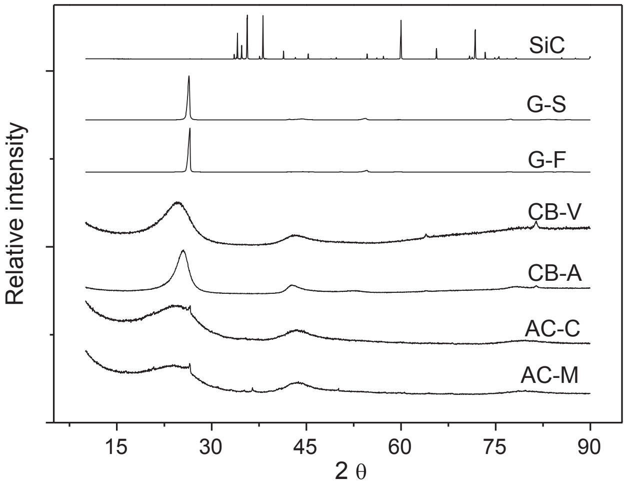


Fig. 1. XRD patterns of the carbon materials.

2. Materials and methods

2.1. Reactants

Phenol was supplied by Sigma-Aldrich and H_2O_2 (30% w/v) by Panreac. The respective aqueous solutions were prepared at pH_0 3 using HCl (37% w/v; Panreac).

Activated carbons were supplied by Merck (AC-M, ref.: 102514) and Chemviron (AC-C), carbon blacks by Alfa-Aesar (CB-A, ref.: 1333-86-4) and Vulcan (CB-V, ref.: CC72R), Graphite from Fluka (G-F, ref.: 1249167) and Sigma-Aldrich (G-S, ref.: 282863) and silicon carbide by Goodfellow (SiC). All these materials were used as received. All samples were supplied in powder, except for ACs, which were grounded and sieved to achieve a particle size < 150 μm.

H_2SO_4 (96 wt%), H_3PO_4 (85 wt%) acetonitrile, $TiOSO_4$, Na_2CO_3 and $NaHCO_3$, supplied by Sigma-Aldrich, were used in the analytic procedure. All reagents are analytical grade and they were used as received without further purification. Working standard solutions of phenol, catechol, resorcinol, hydroquinone, p-benzoquinone, and organic acids (fumaric, malonic, maleic, acetic and formic from Sigma-Aldrich and oxalic from Panreac) were prepared for calibration. Ultrapure water was used throughout the work.

2.2. MW-CWPO experiments

MW-CWPO runs were performed in high pressure PTFE reaction vessels located in a microwave furnace (flexiWAVE, Milestone). The experiments were conducted in batch using 100 mL stoppered PTFE reactors which were initially loaded with aqueous phenol solution (100 mg L^{-1}) at $pH_0 = 3$ and 500 mg L^{-1} of catalyst H_2O_2 was added at 500 mg L^{-1}, corresponding to the theoretical stoichiometric amount for complete mineralization of phenol. Stirring was fixed at 400 rpm, which allowed maintaining the catalyst in suspension and avoiding external mass-transfer limitation. Heating rate was set at 80 °C/min to reach the reaction temperature 120 °C, which was maintained for 15 min. During reaction, the pressure rose up above 2 bar. All the experiments were done by triplicate, being the standard deviation always $< 5\%$.

2.3. Catalyst characterization

The porous texture of the supports and catalysts was characterized by 77 K N_2 adsorption/desorption using a Micromeritics Tristar apparatus. The specific surface area (S_{BET}) and the external or non-microporous area (A_{ext}) were calculated by the BET and t-method, respectively. X-Ray Diffraction (XRD) patterns were obtained in a D5000 X-