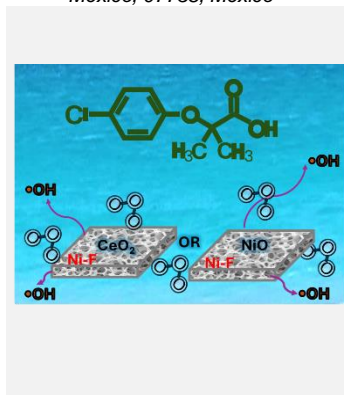


Ni-Foam Bifunctional catalyst for degradation of Clofibrac acid by catalytic ozonation

Short ORAL
Ph.D. Student: Y
Journal: JECE

Daynahi. Franco Peláez¹, Julia Liliana Rodríguez S.¹, Tatiana Poznyak¹, Claudia Jazmín Ramos Torres², Hugo Martínez Gutiérrez²

- (1) Laboratorio de Investigación en Ingeniería Química Ambiental, ESIQIE-Instituto Politécnico Nacional, Zacatenco, Ciudad de México 07738, México. daynahi.fp@gmail.com
- (2) Centro de Nanociencias y Micro y Nanotecnologías. Instituto Politécnico Nacional. Zacatenco, Ciudad de México, 07738, México



Clofibrac acid (CA), an important blood lipid regulatory drug, is considered an emergent organic pollutant present in water sources. The CA degradation in an aqueous solution by catalytic ozonation was investigated. CeO₂ and NiO thin films were deposited by ultrasonic spray pyrolysis on Ni-foam (Ni-F) as substrate. Complete removal of CA was easily obtained by single ozonation and improved in presence of NiO/Ni-F (complete degradation at 10 min). However, the presence of CeO₂/Ni-F catalyst enhanced the TOC removal to 23.5 % at 120 min compared with NiO/Ni-F and alone ozonation. This result may be due to the generation of reactive oxidant species, due the presence of Ce³⁺ and Ce⁴⁺ on the catalyst and oxygen vacancies.

Introduction

Pharmaceutical and personal care products (PPCP) residues in the environment have become a major concern as emerging contaminants due to their potential impact on human health and the ecosystem. Nowadays, thousands of tons of blood lipid regulators are used annually, so they have received much attention [1]. Clofibrac acid (CA) is an active metabolite of anticholesterol, antilipid, and antitumor drugs due to its high toxicity and persistence, thus CA is resistant to biodegradation. More than 60% of hypolipidemic byproducts (e.g., clofibrate, benzofibrate, gemfibezil, etc.) that enter the human body can produce CA during biometabolism, resulting in elevated CA concentrations [2].

Thus, the pharmaceutical industry, commercial wastewater treatment plants (WWTP), hospitals, landfills, human and animal excreta contribute to the environmental accumulation of CA. Although they are present in lowest concentrations (ng/L - mg/L), these will continue to increase, causing a great threat to humans, animals and aquatic organisms. Therefore, it is necessary to find an effective method to remove CA from wastewater.

Advanced oxidation processes (AOP's) involve the generation of nonselective hydroxyl radicals (•OH) which are effective to eliminate refractory organic pollutants from aqueous solution. Among the (AOP's), catalytic ozonation combines the oxidant power of the ozone and the characteristics of metal oxides, metal/metal oxides on supporters and carbon-base materials as catalysts, they can promote ozone decomposition for generating many •OH. Therefore, the synthesis and manufacture of active materials with large specific surface area and porosity es very important. Some researchers have

demonstrated that CeO₂ [3] and NiO [4] presented notable catalytic activity. In this sense, in the present work, thin films of CeO₂ and NiO were deposited onto nickel foam (Ni-F) for evaluated the CA removal using ozone as an oxidant agent.

Material and Methods

Nickel nitrate hexahydrate (Ni (NO₃)₂·6H₂O) (purity 97%), cerium nitrate hexahydrate (Ce (NO₃)₃·6H₂O (purity 99 %), clofibrac acid (purity 97%), ethanol and HCl were purchased from Sigma Aldrich. Nickel foam (thickness: 1mm, surface area: 3.263 m²/g) was purchased from Guangzhou Lige Technology Co., LTD. All chemicals used in the experiment were of analytical grade and were used as received without further purification. Deionized water was used throughout the experiment for the films synthesis and distilled water was used for the clofibrac acid solution.

NiF preparation: NiF pieces of 1 cm x 2 cm and 2 cm x 4 cm were successively immersed in an ultrasonic bath of 1 M HCl, ethanol and deionized water for 30 min to remove stains and surface oxides, respectively. Then, the cleaned NiF was dried at 60 °C for 12h.

Synthesis of the films: NiO and CeO₂ films have been deposited on NiF by ultrasonic spray pyrolysis (UPS) technique at substrate temperature of 450 ± 5 °C. The spraying solutions were prepared by dissolving 0.1 M of Ni (NO₃)₂·6H₂O for NiO films and 0.1 M of Ce (NO₃)₃·6H₂O for CeO₂ films in deionized water and then stirred for 2h at 600 rpm to obtain a homogeneous solution. This solution was transformed into mist using an ultrasonic humidifier operating at frequency of 1.2 MHz. One piece of Ni-F was preheated for 10 min and NiO or CeO₂ was deposited on Ni-F for 15 min, NiO/Ni-F and CeO₂/Ni-F, respectively. The spray-substrate nozzle distance

was fixed at 3.7 cm and the flow of compressed air was 20 psi. Finally, after cooling down to room temperature, the films NiO/Ni-F and CeO₂/Ni-F were stored until further analyses.

Catalytic ozonation test: The catalytic ozonation setup employed in this study includes an ozone generation system, a reactor, thin films, and ozone sensor. Ozone was generated by a standard laboratory ozonizer (HTU500G, Azco Industries Limited, Canada) using high-pure oxygen (99.8 %). The ozone produced was distributed in a reactor by a porous glass plate at the bottom of the reactor. Ozone dosages of 15 mgL⁻¹ were selected for all experiments at 0.2 Lmin⁻¹ ozone flow and CA solution (20±2 mg L⁻¹). The ozone concentration was continuously introduced to the reactor, and the residual ozone in the gas phase was measured with BMT 946 BT (BMT Mess Technik, Berlin) which was simultaneously destroyed using an activated carbon filter. The samples were taken from the reactor at specified intervals for further analysis.

Analytic techniques: The concentrations of CA in aqueous solutions were measured by High-Performance Liquid Chromatography (HPLC, Perkin Elmer Flexar) equipped with a diodes detector at 230 nm and a prevail organic acid column (150x4.6 mm, 5 μm), the flow rate was 1 mLmin⁻¹ with a mobile phase of 60:40 (v/v) acetonitrile: water adjusted at 2.5 pH with phosphoric acid. The total organic carbon (TOC) analyzer was a Shimadzu TOC-500 A to obtain the TOC in solution for samples taken at 120 min.

Results and Discussion

To study the catalytic activity of the Ni-F, the effect of the size used is explored in the catalytic ozonation process, the results show that the presence of Ni-F (0.3 cm³) has around 98% CA removal at 8 min compared with Ni-F (1.2 cm³), which presented completed CA removal at 15 min, Figure 1a, and the difference in the catalytic activity of Ni-F size was observed in the results of TOC removal in 120 min, Figure 1b.

The TOC removal was only a 16% for single ozonation, an 17.5 % for Ni-F (1.2 cm) and 21.5 for Ni-F (0.3 cm³). The Ni-F (0.3 cm³) was chosen to

deposit the thin films of CeO₂ and NiO, the effect of each film on the degradation of CA is presented in Figure 1c.

The results show that the presence of CeO₂/Ni-F and NiO/Ni-F films have a slight effect on the CA removal, the total CA removal was at 10, 15 and 25 min for NiO/Ni-F, single ozonation and CeO₂/Ni-F, respectively.

In figure 1d, for the system with films the TOC removal at 120 min trend is as follow: single ozonation (16%), NiO/Ni-F (23.3%), CeO₂/Ni-F (24.6). It indicates that the single ozonation process has high selectivity for organic matter and cannot effectively mineralize byproducts generated during CA removal.

The bifunctional catalyst can catalyze the further oxidation of some intermediates from the ozonation of AC. Is interesting to note that the best catalytic activity was CeO₂/Ni-F, this may be due the interaction of the interface of CeO₂ and Ni-F to generate electrons that can promote the generation of (•OH) radicals and also the generation of reactive oxidant species, for the presence of Ce³⁺ and Ce⁴⁺.

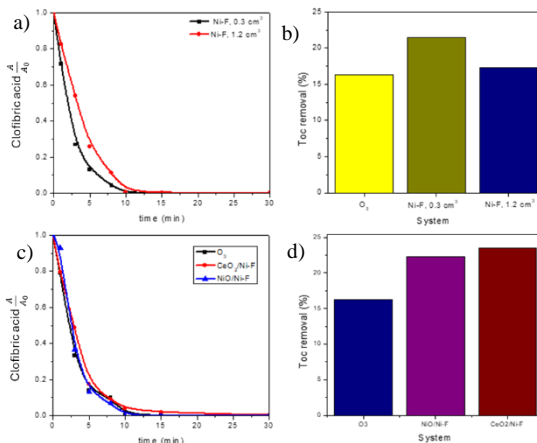


Figure 1. (a,c) Degradation profiles of AC and (b,d) TOC removal in presence of Ni-F, CeO₂/NiF and NiO/NiF.

Conclusions

Thin films of NiO and CeO₂ were successfully synthesized onto Ni-F by ultrasonic spray pyrolysis technique. The presence of NiO/Ni-F and CeO₂/Ni-F increases the TOC removal compared to conventional ozonation and allowed reduces CA removal time (10 min). These thin films can be a promising catalyst for the elimination of emergent pollutants from water using ozone. The films have the main advantage that they are easily recovered from the reaction medium avoiding additional techniques of separation.

Acknowledgments

The authors acknowledge to Consejo Nacional de Ciencia y Tecnología for the PhD scholarship, al proyecto aprobado por el Fondo Sectorial de Investigación para la educación (Project No. A1-S-30591) and Instituto Politécnico Nacional (Projects No. 20240471, Innovation No. 20242857).

References

- [1] Li, W., Lu, S., Qiu, Z., & Lin, K. (2011). UV and VUV photolysis vs. UV/H₂O₂ and VUV/H₂O₂ treatment for removal of clofibrinic acid in aqueous solution. *Environmental technology*, 32(10), 1063-1071. Author, Y. Author, Z. Author, *Journal name*, volume (year) first page.
- [2] Rebelo, D., Correia, A. T., & Nunes, B. (2020). Acute and chronic effects of environmental realistic concentrations of clofibrinic acid in Danio rerio: *Environmental Toxicology and Pharmacology*, 80, 103468.
- [3] I.C. Guzmán, J.L. Rodríguez, T. Poznyak, I. Chairez, I. Hernández, R.T. Hernández, Catalytic ozonation of 4-chlorophenol and 4-phenolsulfonic acid by CeO₂ films, *Catalysis Communications*, 133 (2020) 105827.
- [4] C.M. Aguilar-Melo, J.L. Rodríguez, I. Chairez, I. Salgado, J.A. Andraca Adame, J.A. Galaviz-Pérez, J. Vazquez-Arenas, T. Poznyak, Enhanced Naproxen Elimination in Water by Catalytic Ozonation Based on NiO Films, *Catalysts*, 10 (2020).