Photocatalytic removal of phenol using composites of activated carbon and ferrous oxalate derived from Ecuadorian black sands

ORAL
Ph.D. Student: N
Journal: XXX

V.H. Guerrero[1], *S. Galeas*[1,2], *C.S. Valdivieso*[1], *P.I. Pontón*[1], *V. Goetz*[2], *P. Zárate*[1], *P. Vargas*[1]. *(1) Escuela Politécnica Nacional, Ladrón de Guevara E11-253, 170511 Quito, Ecuador, victor.guerrero@epn.edu.ec. (2) PROMES-CNRS UPR 8521, PROcesses Materials and Solar Energy, Rambla de la Thermodynamique, 66100 Perpignan, France*

In this work, composites made of activated carbon (AC) and ferrous oxalate dihydrate (FOD) were used to degrade phenol present in synthetic waters. For this purpose, 7 g of iron-rich black sands and 5 or 10 g of AC were loaded in a reactor, along with 300 mL of a 1M oxalic acid solution. An environmentally-friendly hydrothermal synthesis was performed in the reactor under subcritical water conditions (135 °C, 12 h). The structure, and morphology of the materials synthesized were determined. The composites obtained (1.5 g/L) were able to remove up to 87% of phenol in water (10 mg/L), after 1 h of adsorption and 6 h of irradiation under visible light. These results illustrate the promising use of low-cost precursors to remove organic contaminants from water using visible light.

Introduction

The continuous and rapid population growth, along with the consequent urbanization and industrialization, has resulted in an accelerated degradation of every environmental compartment [1]. In the case of water, during the last few decades, a relatively large group of substances has been found with higher frequencies and in significant concentrations around the globe. These substances, present not only in wastewaters but also in water bodies, include persistent, and pseudo-persistent contaminants, such as pharmaceutical and personal care products, pesticides, aromatic, chlorinated, brominated and fluorinated compounds, heavy metals, and microplastics. Because of their abundance and toxicity, these substances have potentially harmful effects not only for the environment but also for human health [2]. Therefore, it is essential to develop materials and technologies to remove these water contaminants, avoiding the difficulties commonly found with conventional treatment methods [3].

Adsorption and photocatalysis are among the most effective technologies that can be used to remove a wide variety of organic pollutants that can be found in wastewaters. Adsorption is a relatively simple and highly efficient method to transfer substances from water to the surface of an adsorbent. On the other hand, in photocatalysis, light irradiation can be used to generate electron-hole pairs at the surface of a photocatalyst, which in turn will produce highly reactive radicals that can degrade, and even mineralize, toxic pollutants found in water. Several metal oxides, such as TiO_2, ZnO, Fe_2O_3, and Al_2O_3, have been extensively studied as photocatalysts for wastewater treatment. Despite their relatively high removal efficiency, some of these materials are relatively expensive or difficult to synthesize, show a fast electron-hole recombination that limits their usability, and exhibit a high response within a limited portion of the light spectrum [4]. Therefore, great efforts are dedicated to obtaining low-cost, highly responsive, and efficient materials.

In this work, the removal and degradation of phenol present in synthetic waters was studied, using composite materials. The composites were obtained using activated carbon as a support for ferrous oxalate particles, which were obtained by an environmentally friendly one-step hydrothermal synthesis, employing low-cost Ecuadorian ferrotitaniferous black sands. The adsorptive ability of the composite was tested, along with the photocatalytic degradation of phenol under visible light irradiation.

Material and Methods

Granular activated carbon (AC) and Ecuadorian mineral black sands (BS) were used for obtaining the composites to be studied. The AC was provided by Wildcoast S.A. (Ecuador) and had a size between 500 and 2000 µm. The ferrotitaniferous sands were collected from “El Ostional” beach, in Mompiche, Ecuador (0°29′59″ N 80°2′20″ W). These sands are ilmenite/hematite solid solutions, with an estimated composition $0.6\ (FeTiO_3) \cdot 0.4\ (Fe_2O_3)$ [5]. Oxalic acid dihydrate was provided by DQI S.A. (Colombia), with a 99.0% purity. Phenol with a purity higher than 99.55% was purchased from Sigma-Aldrich.

A one-step hydrothermal synthesis was carried out for obtaining the composites. For this synthesis, 7 g of the BS were loaded in a Berghof BR-500 reactor, along with 5 or 10 of AC, and 300 mL of a 1M oxalic acid aqueous solution. The temperature in the reactor was set at 135 °C, for 12 h, while the stirring was kept at 200 rpm. The composites obtained were characterized by X-ray diffraction, scanning electron microscopy and Raman spectroscopy.

Aqueous solutions with a 10 ppm concentration of phenol were prepared to test the removal of the pollutant. A dosage of 1.5 g/L of the composites prepared were used for this purpose. The concentration of the phenol in the solutions (28 mL) were measured after 1 and 6 h of adsorption, and after 1 h of adsorption and 6 h under the irradiation of an 18 W visible light lamp. The phenol concentrations in the solutions were determined using an Agilent L1120 liquid chromatograph equipped with a C18 column.

Results and Discussion

Depending on the conditions, both ferrous oxalate dihydrate (FOD) and titanium dioxide can be obtained from the hydrothermal processing of ferrotitaniferous black sands. The conditions set in this work were selected to promote the crystallization of FOD particles, while the titanium remained in solution [4]. The synthesis of a predominant phase of FOD, with very small amounts of titanium dioxide, was verified by X-ray diffraction and Raman spectroscopy. Figure 1.a shows the X-ray diffraction pattern for the composite obtained using 5 g of AC, while figure 1.b presents the Raman spectrum for the composite obtained when 10 g of AC were loaded. Note that the peaks in the diffractogram coincide with those of the FOD, which was on the composite surface. On the other hand, the Raman spectrum shows bands that can be assigned to the FOD (119, 206, 247, 523, 915, 1471, 1725 cm^{-1}), rutile (1452, 438, and 608 cm^{-1}) and the AC (1325, 1604 cm^{-1}). It is also worth mentioning that relatively high reaction yields were calculated. These yields were 91.0 and 91.4 %, for the cases in which 5 and 10 g of AC were loaded in the reactor, respectively. The insets exhibit typical micrographs of the corresponding composites.

Table 1 shows the adsorption and photocatalytic removal efficiencies of the materials studied. The composites exhibit a higher efficiency for photocatalytic degradation compared to the adsorptive removal, which is based on the presence of the AC. Note that the photodegradation efficiency observed in the case of phenol is close to the one observed using other similar materials and pollutants [6].

Table 1. Removal efficiencies using AC-FOD composites.

Removal condition	Composite 5 g AC	Composite 10 g AC
Adsorption 1 h	16.1 %	10.8 %
Adsorption 6 h	61.2 %	49.1 %
Adsorption 1 h + photocatalysis 6 h	83.0 %	87.0 %

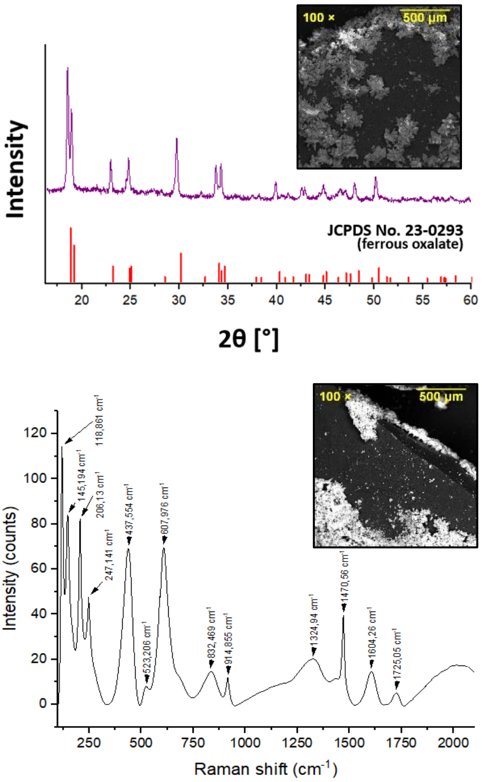

Figure 1. X-ray diffraction pattern (a) and Raman spectrum (b) of the composites obtained with 5 and 10 g of AC, respectively. The micrograph insets illustrate the appearance of the corresponding composites.

Conclusions

The results obtained demonstrate the feasibility of obtaining efficient composite materials with adsorptive and photocatalytic abilities. These composites can be prepared using environmentally friendly methods such as the hydrothermal synthesis in subcritical water conditions, using low-cost abundant mineral precursors. These promising results also open possibilities for the development of materials that could remove organic contaminants using solar light irradiation.

Acknowledgments

The authors thank the financial support for this work provided by the the Escuela Politécnica Nacional, through the project PIM-20-03.

References

[1] G. Devendrapandi et al., *Environ. Res.*, 249 (2024) 118404.
[2] C. Zamora-Ledezma et al., *Environ. Technol. Innov.*, 22 (2021) 101504.
[3] D. Negrete-Bolagay et al., *J. Environ. Manag.*, 300 (2021) 113737.
[4] S. Galeas et al., *Environ. Technol. Innov.*, 32 (2023) 103325.
[5] K. Lagos et al., *Data in Brief,* 32 (2020) 106214.
[6] L. Rao et al., *Mat. Res. Bull.*, 130 (2020) 110919.