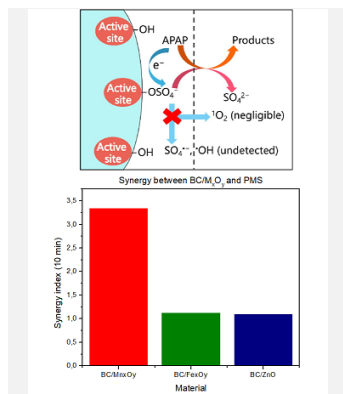


## Carbocatalysis With Biochar/MxOy-based Composites for The Removal of Emerging Contaminants

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Composites based on carbonaceous materials and metal oxides have been used for the removal of emerging contaminants by adsorption or degradation. This is due to their properties that can promote direct oxidation or activate oxidizing agents such as peroxymonosulfate (PMS). In this work, composites were developed from carbonaceous materials from *Zea mays*. (corn stover) and metal oxides of Mn, Fe and Zn; which have been used as carbocatalysts in the degradation of acetaminophen, showing total removal of the pollutant at 10 minutes. Synergy in the carbocatalysis promoted by the three materials was presented.

### Introduction

Transition metals are widely used to activate peroxymonosulfate (PMS) since they do not require high energy consumption to produce hydroxyl and sulfate radicals. PMS can also be activated by carbonaceous matrices, which are of particular interest due to their properties such as high surface area, catalytic properties and thermal stability. Carbonaceous materials have many oxygenated groups and surface defects that can promote reactions of activation of PMS [1].

In the search for materials that promote the catalytic degradation of emerging contaminants, carbonaceous materials have been combined with transition metals, as the latter facilitate the formation of radical species or via non-radical pathways (electron transfer or singlet oxygen) [2,3]. In the presence of metal ions the non-radical pathways can occur via direct degradation mechanism through electron transfer by PMS groups adsorbed on the oxide, or mediated by singlet oxygen (<sup>1</sup>O<sub>2</sub>) [4] attack. Considering the above, the aims of this work is to study the removal of acetaminophen (a pollutant model) from an aqueous matrix using carbonaceous materials modified with metal oxides and peroxymonosulfate as the oxidant agent.

### Material and Methods

The starting material for the preparation of biochar was corn stover (*Zea mays*.) obtained from agricultural residues in Boyacá, Colombia. The biomass suitable for pyrolysis was selected by sieving, with a grain size between 180 and 600 μm. Subsequently, the biomass was heated at a ramp rate of 100°C/h until reaching the activation

temperature (500°C), which was maintained for 2 hours. Then, the prepared biochar (BC) was impregnated in a molar ratio of 1:3 with ZnCl<sub>2</sub>, MnCO<sub>3</sub> and FeCl<sub>3</sub>, and then dried at 120°C for 24 hours. Each material was then calcined at a ramp rate of 100°C/h until reaching 800°C and maintained for 1 hour. Once the BC/M<sub>x</sub>O<sub>y</sub> composites were synthesized, they were washed with 0.1 M HCl or 0.1 M NaOH until reaching a neutral pH when dissolved in distilled water. Subsequently, the materials were filtered, dried, and packed. The evaluation of the efficiency and degradation mechanisms of ACE were investigated to verify the adsorption and catalytic activity of biochar and composites. For this purpose, 0.2 g/L of the materials were added to a 400 mL reactor containing a solution with 30.6 μmol L<sup>-1</sup> of ACE. Then, for adsorption tests, mechanical stirring at 120 rpm for 50 minutes and aliquots of 1 mL were taken at certain time intervals. Likewise, for carbocatalysis tests, PMS was added to the reaction vessel solution at a final concentration of 500 μmol L<sup>-1</sup>. In all cases, aliquots were filtered with 0.45 μm filters in amber vials, and drug concentrations were determined HPLC with specific UV detection [5].

The synergy index (S) for the carbocatalytic system was determined using Eq. 1, where %R corresponds to the percentage of removal induced by the processes (S = 1, additive; S < 1, antagonistic, S > 1, synergistic).

$$S = \frac{\%R_{\text{Carbocatalysis}}}{\%R_{\text{Oxidation}} + \%R_{\text{Adsorption}}} \quad (1)$$

### Results and Discussion

Different phenomena are observed in the removal

of acetaminophen depending on the material

used. The carbonaceous material by itself showed to be inefficient to remove the contaminant either by adsorption or degradation. On the other hand, in the BC/Mn<sub>x</sub>O<sub>y</sub> material, the removal of the contaminant by adsorption was not effective. However, when PMS was added to the system, contaminant degradation was achieved in approximately 10 minutes ( $S_{10} = 3.34$ ), which indicated that a) the material can activate peroxymonosulfate and eliminate the pollutant via a radical or non-radical route or b) there is a direct electronic transfer via PMS groups adsorbed on the oxide. The porosity of the material is low, which can be seen in the adsorption isotherm (Fig 1e). In the case of the materials BC/Fe<sub>x</sub>O<sub>y</sub> ( $S_{10} = 1.12$ ) and BC/ZnO ( $S_{10} = 1.09$ ), both showed similar behavior in terms of adsorption and

synergy at 10 minutes. The low synergy observed for BC/Fe<sub>x</sub>O<sub>y</sub> and BC/ZnO can be attributed to their good adsorbent properties. This was confirmed with their respective adsorption isotherms (Figs 1f and 1g), where the BC/Fe<sub>x</sub>O<sub>y</sub> material presented a type II isotherm, indicating the coexistence of micropores and mesopores. While, the BC/ZnO material showed a Type I isotherm, typical of microporous materials, which explains its high adsorptive capacity based on a large surface area. The pore distribution histograms (Fig 1a, 1b and 1c) show that, for all three materials, micropores (<20Å) are present, which may contribute to an anchoring of the molecules, which can be oxidized by direct electronic transfer or by radical mechanisms.

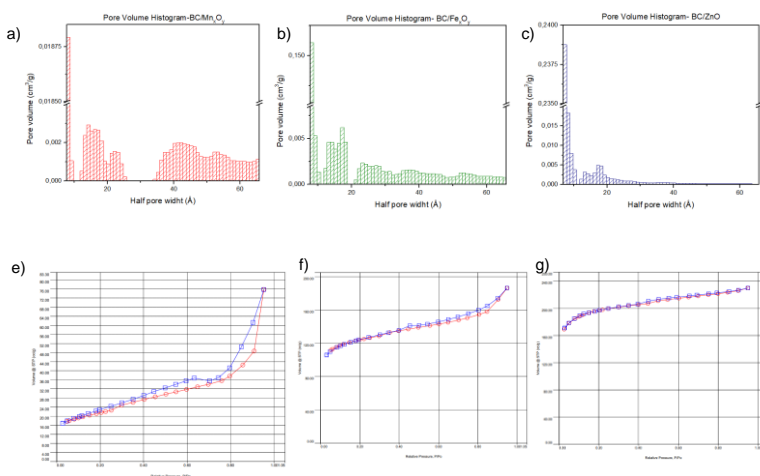


Fig 1. Pore Volume Histograms of: a) BC/Mn<sub>x</sub>O<sub>y</sub>, b) BC/Fe<sub>x</sub>O<sub>y</sub>, c) BC/ZnO. Adsorption-Desorption isotherms of: e) BC/MnO, f) BC/Fe<sub>x</sub>O<sub>y</sub>, g) BC/ZnO

### Conclusions

Composites based on biochar obtained from lignocellulosic wastes from corn stover and metal oxides were synthesized. These materials showed to be efficient in the removal of acetaminophen from water. Synergy was found in the degradation of pollutants by combining the composites and PMS, particularly for BC/MnO.

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