Combination of photo-Fenton and adsorption processes for removal of sulfonamides using iron-modified biochars

POSTER
Ph.D. Student: N
Journal: CEJ

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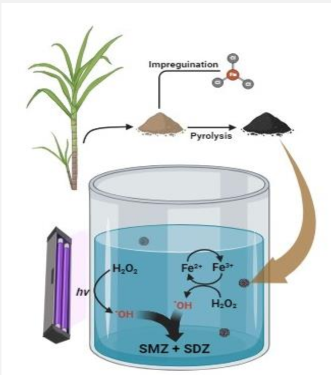

This study explores the potential of AOPs in the treatment of resistant contaminants, emphasizing the synergistic effect of adsorption and heterogeneous Fenton oxidation. Biochar based on sugarcane bagasse modified with iron ions was evaluated as a catalyst for the simultaneous degradation of the antibiotics sulfadiazine (SDZ) and sulfamethazine (SMZ). The preparation involved iron impregnation, in a one-step synthesis, then pyrolysis to obtain an iron modified biochar (BC:Fe). The characterization revealed that BC:Fe has a smaller specific surface area due to the accumulation of iron oxide, but showed crystallinity compatible with the formation of magnetite. The adsorption tests revealed a 25% removal efficiency of SDZ and SMZ on BC:Fe (0.05 g L^{-1}), while the photo-Fenton process with BC:Fe achieved over 80% removal after 120 min (5 mmol L^{-1} H_2O_2 and UV irradiation at pH 6). The BC:Fe proved to be efficient for the removal of recalcitrant contaminants, combining adsorption with photo-Fenton oxidation processes.

Introduction

The combination of the adsorption process and heterogeneous Fenton oxidation can favor the action of in situ generated hydroxyl radicals [1]. In addition, the high carbon content of biochars promotes chemical and thermal stability, which is beneficial for improving interaction with active sites[2][3]. The aim of this study was to investigate the adsorptive and catalytic properties of a sugarcane bagasse-based biochar impregnated with iron oxide for the heterogeneous photo-Fenton degradation of the antibiotics sulfadiazine (SDZ) and sulfamethazine (SMZ) simultaneously, which are reported to be recalcitrant compounds[4][5].

Material and Methods

The Fe-modified biochar composite (BC:Fe) was prepared using the impregnation method, for which 30 g of dried sugarcane bagasse was mixed with 250 mL of a 0.125 mol L^{-1} aqueous $FeCl_3$ solution. After four hours of constant stirring, the mixture was filtered, dried at room temperature and subjected to pyrolysis at 800 °C for 2 hours at a heating rate of 5°C min^{-1} to obtain Fe-modified biochar (BC:Fe). The same procedure was carried out to obtain biochar without iron impregnation (BC). The materials obtained were characterized by thermogravimetric analysis (TG) and X-ray diffraction, while Brunauer - Emmett - Teller (BET) specific area was obtained by N_2 adsorption-desorption measurements. The adsorption properties and catalytic activity of BC:Fe and BC materials were evaluated for the simultaneous removal of the antibiotics sulfadiazine (SDZ) and sulfamethazine (SMZ) from 250 mL of aqueous solution containing 2 µmol L^{-1} each, in presence or absence of 5 mmol L^{-1} hydrogen peroxide, with and without UV irradiation (30 W). The experiments were carried out at pH 6, with 0.05 g L^{-1} of the, in a bench-scale reactor under magnetic stirring. Degradation was monitored by high-performance liquid chromatography coupled to a diode array detector (HPLC/DAD) after filtration through a 0.22 µm PVDF membrane. Isocratic elution was carried out with methanol/water (25/75, v/v) at a flow rate of 1 mL min^{-1}, an injection volume of 40 µL and a detection wavelength of 262 nm. Under these conditions, the retention times for SDZ and SMZ were 4.5 and 9.7 min, respectively.

Results and Discussion

The N_2 adsorption-desorption isotherms and the pore diameter distribution of the prepared materials showed H1 hysteresis, which exhibits the type IV isotherm model according to the IUPAC classification; this type describes the adsorption behavior of a specific mesoporous material. The specific area of BC:Fe and BC biochar was 291.4 and 349.9 m^2 g^{-1}, respectively. The lower area of BC:Fe is probably due to the accumulation of iron oxides in the pores of the biochar. The XRD data for BC showed diffraction peaks at 23° that reveal the presence of an amorphous carbon structure (002) in the biochar, while the BC:Fe biochar showed crystallinity with diffraction peaks at 30.2° (220), 35.5° (311), 43.2° (400) and 56.9° (511), attributed to the formation of magnetite. The presence of magnetite results in magnetic properties, which favor easy separation after its use in wastewater treatment. In addition, it contributes to the thermal stability verified by thermogravimetric analysis at 800 °C, observing a residual weight of 85% with iron (BC:Fe) and 77% without iron (BC), demonstrating that the presence of iron oxides reduces the initial and final decomposition temperatures. These characteristics clearly show the influence of iron oxides on the physical and chemical structure of biochar. The application of biochar without iron resulted in 25% adsorption of SDZ and SMZ after 30 min using 0.05 g L^{-1} (Fig.1b).

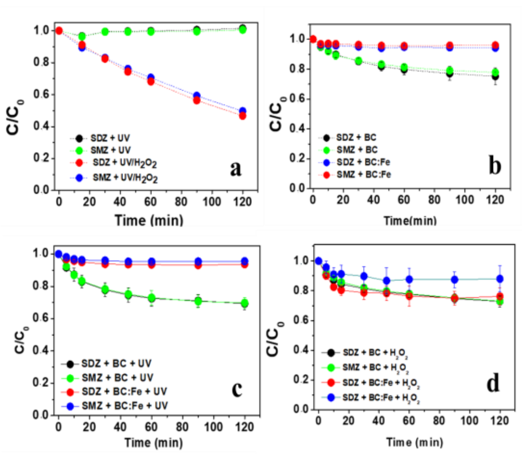

Figure 1: Removal of SDZ and SMZ by: a) direct photolysis and UV/H_2O_2; and removal using BC and BC:Fe biochars by b) adsorption; c) irradiation d) dark Fenton. Conditions: SMZ = SDZ = 2 µmol L^{-1}; pH 6; catalyst = 0.05 g L^{-1}.

When BC was applied in the presence of 5 mmol L^{-1} of H_2O_2 in the dark, less than 25% of both antibiotics were removed after 120 min, very similar to that obtained by adsorption. The BC:Fe biochar showed an adsorption equivalent to 3% (Fig. 1b), but in the presence of H_2O_2 (dark Fenton) (Fig. 1d) a removal of 23% after 40 min was observed, resulting from the action of hydroxyl radicals generated by the decomposition of H_2O_2 on the surface of the iron modified biochar. The UV irradiation data demonstrated the absence of significant direct photolysis for SDZ or SMZ (Fig. 1a). However, with the addition of H_2O_2 (UV/H_2O_2) more than 50% removal was observed after 120 min (Fig.1a). This behavior can be attributed to the formation of radical species by the decomposition of hydrogen peroxide under UV light. The irradiation of BC and BC:Fe biochars in the absence of H_2O_2 resulted in a removal similar to that due to the adsorption process, which means that the materials did not show photocatalytic activity. However, when BC:Fe was applied in the presence of H_2O_2 under irradiation (heterogeneous photo-Fenton combined with adsorption) (Fig. 2), simultaneous removal of the antibiotics reached more than 80% after 120 min, denoting the efficiency of the process under irradiation.

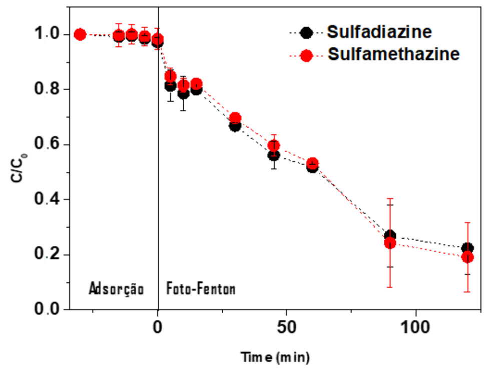

Figure 2: Simultaneous removal of SDZ and SMZ in a combined adsorption and photo-Fenton process using BC:Fe biochar as catalyst. Conditions: SMZ = SDZ = 2 µmol L^{-1}; pH 6; catalyst = 0.05 g L^{-1}.

Conclusions

The BC:Fe biochar prepared in a one-step method with sugar cane bagasse as raw material presents high specific surface area, even with magnetite incorporated, which confered magnetic properties. It promoted 3% adsorption of SDZ and SMZ following simultaneous degradation by photo-Fenton, which achieved over 80% removal at pH 6. These results indicate the potential of application of the iron modified biochar for the removal of recalcitrant contaminants by combining the adsorption process on biochar with photo-Fenton oxidation.

Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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