Enhanced Removal of Sulfonamides Using Heterogeneous Fenton Processes Coupled with Basic Activated Biochar Adsorption

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The study examined Fe-modified biochar with KOH activation for removing SDZ and SMZ antibiotics. XRD analysis indicated magnetite formation in BC:Fe:KOH, enhancing crystallinity. FT-IR spectra showed increased oxygen-containing functional groups after KOH activation, improving adsorption capacity. BC:Fe:KOH exhibited a 20% increase in specific surface area compared to BC:Fe. Adsorption with the BC:Fe:KOH showed a total removal of the substances in less than 20 minutes. Combining photo-Fenton with adsorption led to simultaneous reaction and degradation of 90% of the substances being degraded in 90 minutes with activated biochar (0,05 g L^{-1}). The study underscores the efficacy of Fe-modified biochar with KOH activation in mitigating emerging pollutant contamination in water bodies.

Introduction

Sulfadiazine (SDZ) and sulfamethazine (SMZ) are antibiotics commonly used in veterinary medicinefor treating livestock diseases and promoting growth in animals [1]. Due to their toxicity, presence in water bodies, and bioaccumulation, these substances are considered emerging pollutants. Conventional wastewater treatment processes, such as coagulation and membrane separation can partially remove these substances, but a significant portion persists and is released into the environment [2]. Therefore, the use of advanced oxidation processes, especially heterogeneous Fenton reactions, coupled with adsorption using biochar from agricultural residues such as sugarcane bagasse after pyrolysis, presents a low-cost material with good separation efficiency and no transformation product [3,4]. The catalytic activity of activated carbon depends on chemical surface, and chemical activation not only improves specific surface area but also the presence of functional groups in biochar[5]. Among activators, KOH favors surface area enhancement, reacting with oxygen-containing functional groups during activation. Additionally, modifications of biochar with iron oxides incorporation, acting as catalysts, enable easy removal of the adsorbent from the aqueous medium through magnetic separation technologies. Thus, this study aims to evaluate the influence of KOH activation through the physicochemical properties and morphology of the material, and on the removal of sulfadiazine and sulfamethazine together with adsorption and photo-Fenton.

Material and Methods

The Fe-modified biochar (BC:Fe) with and without KOH activation were prepared using the impregnation method, where 30 g of dried sugarcane bagasse was mixed with 250 mL of an aqueous solution containing 0.125 mol L^{-1} $FeCl_3$. 100 ml of 0.2 mol L^{-1} KOH was added in BC:Fe:KOH. After four hours of continuous stirring, the mixture was filtered, dried at room temperature (25 °C), and subjected to pyrolysis at 800 °C for 2 hours, with a heating rate of 5°C min^{-1}, to produce Fe-modified biochar with and without KOH activation (BC:Fe:KOH). The resulting materials were characterized by X-ray diffraction, while the specific surface area was determined through N_2 adsorption-desorption measurements, and Fourier-transform infrared spectroscopy (FT-IR) was used to characterize functional groups. The adsorption properties and catalytic activity of BC:Fe:KOH 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, varying parameters such as the presence or absence of 5 mmol L^{-1} hydrogen peroxide, with and without 30 W UV irradiation. The experiments were conducted at pH 6, with a catalyst dosage of 0.5 g L^{-1}, in a bench-scale reactor with 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 performed with a mobile phase of methanol/water (25/75, v/v) at a flow rate of 1 mL min^{-1}, with an injection volume of 40 µL and 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

XRD analysis showed that the biochar has an amorphous structure. After modification with iron oxides and activation using KOH, diffraction peaks at 30.2°C (220), 35.5°C (311), 43.2°C (400), and 56.9°C (511) were identified, which suggest crystallinity resulting from magnetite formation in BC:Fe:KOH (Fig. 1a). Subsequently, during thermal treatment, $Fe(OH)_3$ is mostly transformed into magnetite, along with the remaining Fe^{2+} species. Additionally, FT-IR absorption peaks related to OH, CH, C=O, CO and COC provides information about OH groups between 2800 and 3500 cm^{-1}, with an increase of C-O stretching peaks at 1050 cm^{-1}. These peaks indicate that after BC activation with KOH formation of oxygen-containing functional groups occurs (Fig. 1b). The specific surface area of BC:Fe:KOH was 394.9766 m^2g^{-1} compared to BC:Fe, which was 291.3937 m^2g^{-1}, representing a 35.5% increase in the specific surface area with KOH activation.

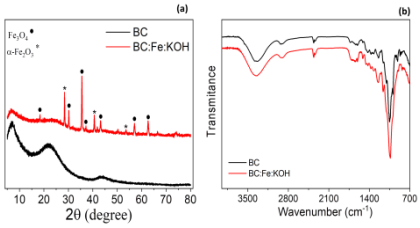

Fig. 1. Characterization data of sugarcane biochar with and without basic activation using KOH. (a) X-ray Diffratrograms and (b) FT-IR spectra.

Figure 2a depicts adsorption experiments conducted using 0.5 g L^{-1} catalyst, achieving complete adsorption of the SMZ and SDZ in 15 minutes and 45 minutes for BC:Fe:KOH and BC:Fe, respectively. This is consistent with the specific surface area of the material. Due to the rapid adsorption of the antibiotics onto the material, it was necessary to assess the influence of the Fenton process on the degradation of these substances using a lower amount of catalyst (0.05 g L^{-1}). Using 0.05 g L^{-1} catalyst, the photo-Fenton process was applied after BC:Fe:KOH and BC:Fe reached adsorptive stability in 30 minutes (Fig. 2b). Activated biochar showed a 20% increase in degradation compared to BC:Fe, suggesting that mass transfer on the surface of the activated material promotes greater interaction of the substances with hydroxyl radicals compared to BC:Fe, with 90% of the substances being degraded in 90 minutes with activated biochar. Thus, the combination of adsorption with heterogeneous Fenton process demonstrates efficacy in removing sulfadiazine and sulfamethazine form aqueous samples.

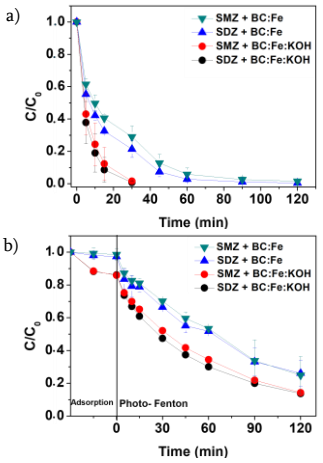

Fig. 2. Simultaneous removal of SMZ and SDZ using iron-modified biochar with and without basic activation: (a) Adsorption with 0.5 g L^{-1} catalysts, and (b) Adsorption combined with photo-Fenton with 0.05 g L^{-1} catalysts.

Conclusions

This study highlights the effectiveness of combining Fe-modified biochar with KOH activation for the removal of sulfadiazine and sulfamethazine antibiotics. The modified biochar exhibited enhanced adsorption capacity compared to single biochar due to increased specific surface area and the presence of functional groups. Additionally, catalytic activity facilitated rapid antibiotic degradation, particularly when coupled with UV irradiation and hydrogen peroxide. These findings suggest a promising approach for addressing emerging pollutant contamination in water bodies, offering a cost-effective and efficient solution.

Acknowledgments

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