EFFECT OF BALL-MILLING AND WATER MATRICES ON THE DEGRADATION OF TRIMETHOPRIM BY BIOCHAR-ACTIVATED PEROXYMONOSULFATE

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ABSTRACT

Antibiotics play an important role in protecting human and animal health from microbial infections. One of the five most commonly used antibiotics in the world is trimethoprim (TMP) that has been detected in river water (up to 60 ng L^{-1}), surface water (25 µg L^{-1}), hospital wastewater (10 µg L^{-1}), and municipal wastewater (0.17–8.8 µg L^{-1}). TMP cannot be completely removed by conventional biological wastewater treatment techniques; hence; poses a risk to humans and the environment. Therefore, the removal of TMP requires a straightforward and efficient method. Advanced persulfate-based oxidation processes (PS-AOPs) are known for their strong oxidative degradation capacity due to the formation of various reactive species, such as HO•, $SO_4^{\bullet-}$ and $^1O_2$. In PS-AOP, carbon-based materials, such as biochars, are emerging catalysts for the activation of various oxidizing agents and the generation of radicals.

In this work, various biomasses (grass pallets (GP-BC), corn cobs (CC-BC), and poplar wood (PW-BC)) were used as raw materials for biochar preparation. The biomass was treated at 400, 500, 600, and 700 °C in an N_2 atmosphere. The particle size of the prepared biochar was decreased with ball milling. Raman and FT-IR spectroscopy performed the characterization of biochars, while the specific surface area was determined via N_2 adsorption. The effectiveness of biochars on peroxymonosulfate ion (HSO_5^-, PMS) as oxidizing agent was investigated in TRIM transformation. The effect of biochar dose, PMS concentration, and biologically treated domestic wastewater as a matrix on the degradation of TRIM was investigated. The potential of GP-BC to activate hydrogen peroxide (H_2O_2) and peroxydisulphate (PDS) was also studied. The effect of pyrolysis temperature on the activity of GP-BC was examined. The specific surface area of biochar and its adsorption capacity decreased with the increase in the pyrolysis temperature from 400 to 700 °C. Still, the efficiency of TRIM transformation increased due to the structural change and depended on biomass as raw material. The ball milling increased the specific surface area of biochar prepared at 700 °C, from 10 m^2/g to 228 m^2/g, 236 m^2/g, and 130 m^2/g for CC-BC, PW-BC, and GP-BC, respectively. As a result, the TRIM ($5{,}0\times10^{-5}$ M) adsorption was negligible before ball milling; however, it increased to 33%, 28%, and 29% for ball-milled CC-BC, PW-BC, and GB-BC, respectively. The adsorptive removal and degradation were achieved up to 78%, 71%, and 93% with a 2.0 mM PMS and 3000 mg/L biochar dose in 120 minutes without ball-milled CC-BC, PW-BC, and GP-BC respectively. The ball-milling highly enhanced the efficiency of PMS activation, and decreased the required

biochar (500 mg/L) and PMS dose (0.2 mM). The overall removal of 83%, 75% and 88% was achieved within 60 minutes for ball-milled CC-BC, PW-BC, and GP-BC respectively. The ball-milled GP-BC was less effective in activating PDS and H_2O_2, so only 17% and 14% TRIM removal were achieved even with the same dose of BC (500 mg/L) and oxidant (0.2 mM).
The effect of various radical scavengers proved that the HO•, $SO_4^{\bullet -}$ and $^1O_2$ plays an important role in the transformation of TRIM. The degradation of TRIM was significantly impeded in biologically treated waste water (BTWW) containing organic substances and inorganic components. The matrix components affect the adsorption of TRIM, and consequently hinder its reaction with reactive species on the surface of biochar. Moreover, organic substances and inorganic ions can behave as HO• and $SO_4^{\bullet -}$ scavengers. Humic acid and HCO_3^- significantly reduced the TRIM transformation efficiency, while the effect of Cl^- was moderate.
In conclusion, the process of ball-milling and temperature have significantly changed the adsorption and degradation properties of biochar. Biologically treated wastewater and inorganic ions, however, have the potential to reduce the overall removal efficiency. The adsorption properties and activity of biochar are greatly impacted by the type of biomass, and temperature of the pyrolysis. By further modifying GP-BC, increased activation of PMS, PDS, and H_2O_2 can be achieved, and the matrix effect can be partially eliminated or reduced.

Keywords: Biochar, trimethoprim, sulfate-based advanced oxidation process, water treatment

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