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Synthesis of iron and nitrogen co-doped biochar for the activation of peroxymonosulfate to degrade sulfamethoxazole

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Abstract: In this study, iron and nitrogen co-doped biochar (Fe-N-BC) was synthesized by a facile pyrolysis process of mixed walnut shell, melamine, and iron(III) chloride, and then the biochar (BC), nitrogen-doped biochar (N-BC), and iron-doped biochar (Fe-BC) also were prepared as a control. The Fe-N-BC demonstrated an excellent degradation performance (0.5 min^{-1}) for sulfamethoxazole (SMX) in the presence of peroxymonosulfate (PMS) compared with BC (0.026 min^{-1}), N-BC (0.038 min^{-1}), and Fe-BC (0.33 min^{-1}). Ultra-high performance liquid chromatography in conjunction with high-resolution mass spectrometry (UHPLC-QTOF-MS) was also used to identify the transformation products of SMX during the degradation process, and the predicted toxicity results from Toxicity Estimation Software Tool (T.E.S.T) exhibited that the overall toxicity of the degradation products lower than SMX.

Keywords: Iron and nitrogen co-doped biochar; peroxymonosulfate; mechanisms; toxicity.

1. Introduction

Advanced oxidation processes (AOPs) are currently considered to be an effective technology for treating emerging contaminants in wastewater. Sulfate radicals ($SO_4^{\cdot-}$) produced during the activation process of peroxymonosulfate (PMS)-based AOPs have drawn the most interest and attention among all AOPs due to their exceptional qualities, which include a high redox potential (E^0 = 2.5–3.1 eV), a longer half-time period (30–40 s), and high efficiency over a broad pH range. It has also been reported that the activation of PMS by carbonaceous materials was a relatively simple, economic, and green process compared with other activation processes (e. g. ultrasound, heat, microwave, and UV). Biochar (BC) is a typical type of carbon-rich material derived from the pyrolysis of biomass under limited or no oxygen conditions, and it can also act as a catalyst for the activation of PMS in the wastewater treatment applications. However, the efficiency of the pristine BC is still limited for the degradation of recalcitrant organic pollutants. In this regard, doping with organic or inorganic elements into BC can be a facile and efficient method to solve this issue. Inspired of this, it's highly expected that the iron, nitrogen co-doped BC displays a high specific surface area, abundant surface functional groups, and excellent degradation performance for organic pollutants.

In this study, the iron, nitrogen co-doped BC (Fe-N-BC) was synthesized through a facile pyrolysis process, and the pristine BC, nitrogen-doped BC (N-BC), and iron-doped BC (Fe-BC) were also prepared as a control. The BCs were employed for the degradation of sulfamethoxazole (SMX) in the presence of PMS. The degradation products and pathways were proposed through the Q-TOF MS analysis.

2. Materials and method

2.1. preparation of nanomaterials

The walnut shell was obtained from Matthys Bvba (Belgium) with a size of around 450-800 µm. The Fe-N-BC was synthesized by a facile pyrolysis method. In a typical process, walnut shell, melamine, and Iron(III) chloride were dispersed into water. After stirring for 24 h, the suspension was put in an oven at 60 °C overnight. The obtained solid was put in the tube furnace at 700 °C with a heating rate of 5 °C/min and held for 2 h at 700 °C. After cooling down to room temperature, the black powder was collected and crashed for further use and characterization. All the pyrolysis processes were carried out under the nitrogen atmosphere. Moreover, the BC, N-BC, and Fe-BC were fabricated through the same preparation process as a comparison.

2.2. Degradation experiments

Batch experiments were conducted in a glass beaker at room temperature. Typically, a certain amount of nanomaterials and PMS solution was introduced to 200 mL of SMX solution. Following that, the samples were extracted at predefined time intervals and filtered through a 0.45 um filter then quenched immediately with an excess $Na_2S_2O_3$ solution. The SMX concentrations were measured by high-performance liquid chromatography (HPLC) with a C18 column (Agilent Eclipse Plus, 4.6 × 250 mm, dp= 5 µm) and a UV-detection wavelength of 254 nm. The mobile phases included the water (solution A) and acetonitrile (ACN, solution B). The elution method consisted of a gradient process, increasing linearly from 10% B to 95% B in 10 min, and held for 1 min, then returned to the initial conditions in 4 min. The flow rate, column temperature, and injection volume were 0.8 mL/min, 35 °C, and 30 µL, respectively.

The degradation efficiency and degradation kinetics rate of SMX were calculated according to Eq. 1-2.

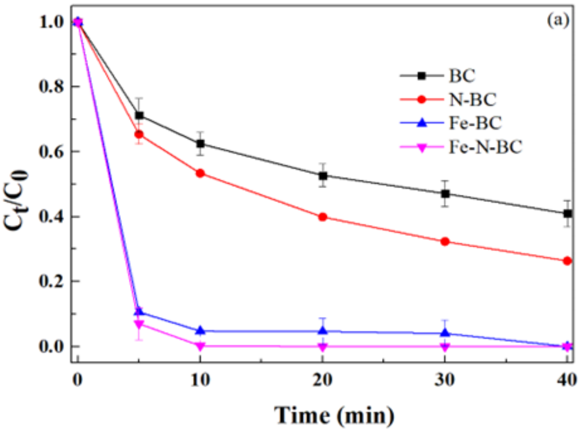
$$\text{Degradation efficiency (\%)}=100\times((C_0-C_t)/C_0) \qquad (1)$$

$$\ln(C_t/C_0)=-K_{obs}\times t \qquad (2)$$

where C_0 and C_t are the SMX concentrations at the initial and reaction time (t), respectively. K_{obs} is the pseudo-first-order reaction rate constant (min^{-1}).

3. Results and discussion

The degradation performance of SMX by the prepared nanomaterials was examined through the activation of PMS. As illustrated in Fig. 1a, the BC represents a relatively low removal efficiency of 60% for SMX in 40 min (0.026 min^{-1}). The N-BC exhibits a higher removal efficiency of 74% for SMX in 40 min (0.038 min^{-1}) than that of BC. It can be confirmed that the N-BC has a high degradation efficiency for SMX in this system. This phenomenon can be explained by the following aspects. First, the rich defects and abundant nitrogen-containing functional groups (such as C≡N) of BC can accelerate the electron transfer in the medium. Second, the higher specific surface area of N-BC can provide more active sites for the degradation of contaminants. In addition, the Fe-BC demonstrates an excellent degradation kinetics rate constant of 0.33 min^{-1} for SMX, which can be associated with the iron oxides playing an important role for the activation of PMS to degrade organic pollutants. Moreover, the Fe-N-BC represents the highest degradation kinetics rates of 0.5 min^{-1} for the SMX among all the prepared nanomaterials. This can be attributed to the fact that the synergistic effects of co-doping of iron and nitrogen in BC. The Fe-N-BC with a large specific surface area can provide more active sites for the activation of PMS, and the iron-containing nanomaterials can efficiently activate PMS. Hence, sufficient active species (e.g. ·OH, $O_2^{\cdot-}$, $^1O_2$) are generated in the medium, resulting in an excellent degradation performance of SMX in such a system.



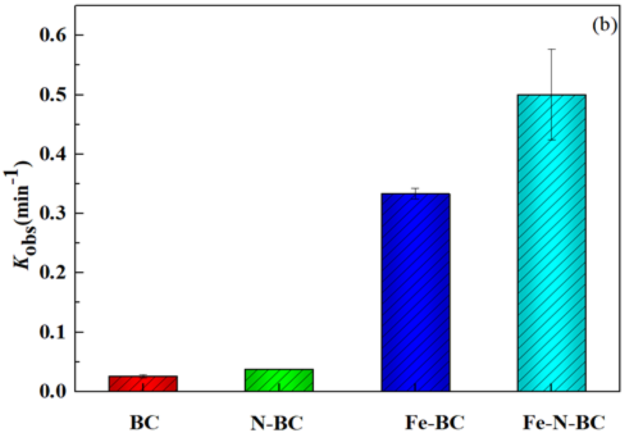


Figure 1. The degradation efficiency (a) and reaction rate constants (b) of SMX by different nanomaterials (conditions: 0.5 g/L catalyst, 1mM PMS, 10mg/L SMX).

The transformation products (TP) of SMX during the degradation process in the Fe-N-BC/PMS system were identified by UHPLC-QTOF-MS. The proposed degradation pathways were also illustrated in Fig. 2. The TP1 was generated through a polymerization effect between two SMX molecules. The TP2 can also be formed by a carboxyl substitution reaction. In addition, TP3 and TP4 were produced through the oxidation of nitroso and methyl of SMX, respectively. The formation of TP5 mainly due to the oxidation and open ring reaction of the isoxazole ring of SMX.

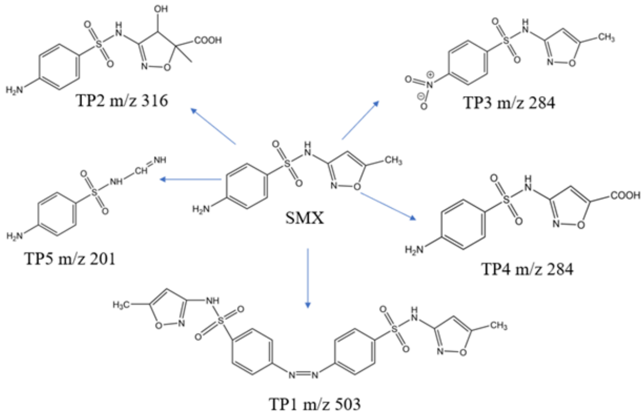


Figure 2. Proposed degradation products and possible degradation pathways for SMX in the Fe-N-BC/PMS system.

As shown in Fig. 3, the toxicity of SMX and its degradation products were evaluated by T.E.S.T based on acute toxicity, bioconcentration factor, developmental toxicity, and mutagenicity. Fig. 2a demonstrates that the acute toxicity of TP2, TP3, TP4, and TP5 decreased to a harmful or not harmful level, while TP1 displays higher acute toxicity than SMX. All the degradation products also display a significant decrease in bioconcentration factor compared with SMX. In addition, SMX and all the degradation products demonstrate developmental toxicity, but the index value of TP1, TP3, and TP5 decreased. The SMX and all the degradation products show negative mutagenicity. Therefore, it can be concluded that the overall toxicity of degradation products decrease compared with SMX, while some of the transformation products have high toxicity and need care during the degradation process.

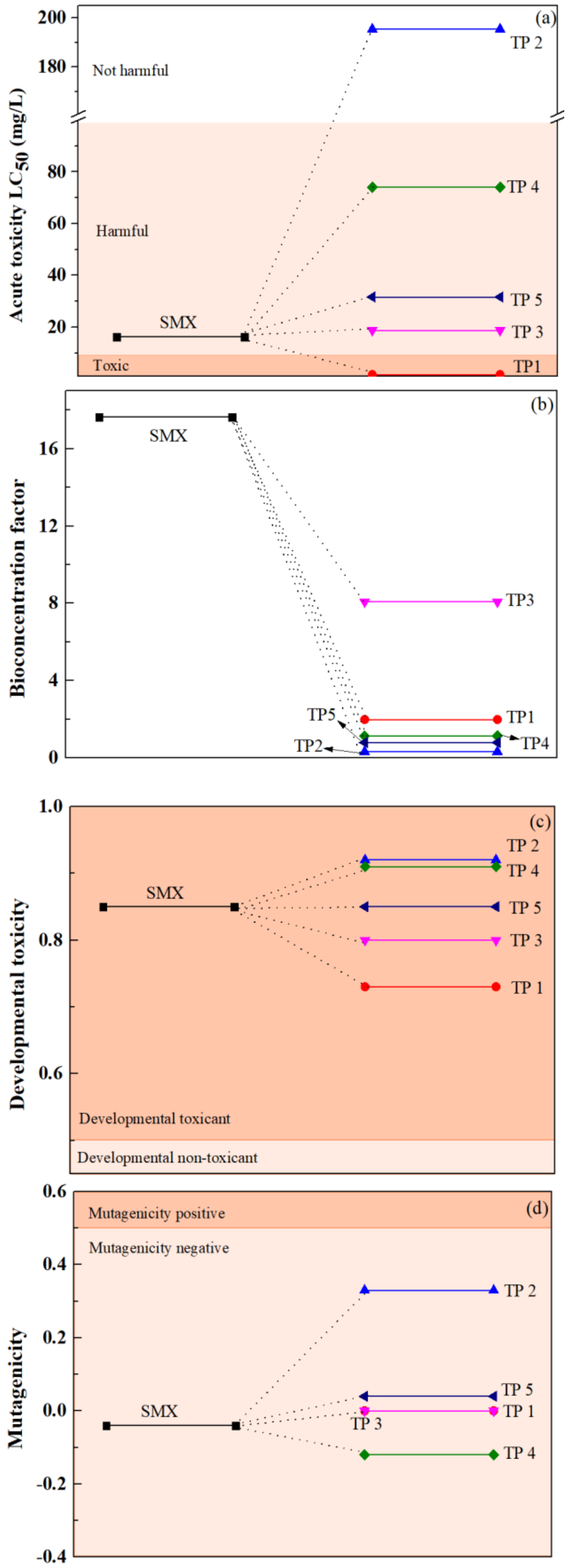


Fig. 3. Acute toxicity (a); bioconcentration factor (b); developmental toxicity (c); mutagenicity (d) of SMX and its degradation products.

4. Conclusions

In this study, the biochar (BC), nitrogen-doped biochar (N-BC), iron-doped biochar (Fe-BC), and iron, nitrogen co-doped biochar (Fe-N-BC) were synthesized through a facile method for the activation of peroxymonosulfate (PMS) to degrade sulfamethoxazole. The Fe-N-BC demonstrates the highest degradation efficiency (0.5 min^{-1}) for SMX in the presence of PMS compared with BC (0.026 min^{-1}), N-BC (0.038 min^{-1}), and Fe-BC (0.33 min^{-1}). Furthermore, the great potential of Fe,N co-doped biochar and provided valuable insight into the synthesis of highly efficient carbon-based catalysts for environmental applications.

5. References

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