Chemical Engineering Journal 356 (2019) 341–349

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Insights into sulfamethazine adsorption interfacial interaction mechanism on mesoporous cellulose biochar: Coupling DFT/FOT simulations with experiments

Quan Chen[a], Jiewei Zheng[a], Jianchang Xu[a], Zhi Dang[b], Lijuan Zhang[a,*]

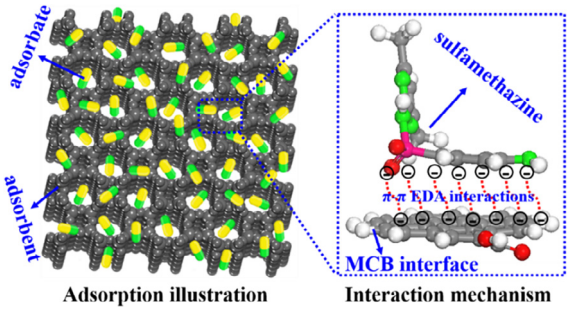
[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China

HIGHLIGHTS

- Insights into SMT adsorption interfacial mechanism on MCB were elaborated.
- The structure-performance relationship in SMT adsorption was elucidated.
- SMT was adsorbed by MCB in the V-shape configuration through π-π EDA interaction.
- Increasing the pyrrole rings content of the adsorbent could enhance SMT adsorption.

GRAPHICAL ABSTRACT

GA Illustration of SMT adsorption onto mesoporous cellulose biochar (MCB) and interfacial interaction mechanism.



ARTICLE INFO

Keywords:
Biochar
Sulfonamide antibiotics
Interfacial micro-mechanism
Frontier orbital theory
Density functional theory

ABSTRACT

Sulfonamide antibiotic contamination promotes the generation of resistance genes, whereas its removal remains a great challenge due to the lack of understanding in its removal micro-mechanism and efficient adsorbents. In this study, the interfacial interaction mechanism associated with the adsorption of sulfamethazine (SMT) on mesoporous cellulose biochar (MCB) adsorbents were studied, as well as the influences of pH value, cations and humic acid (HA) on this interfacial interaction mechanism. A π-electron interaction, not electrostatic interactions, is the main interfacial interaction mechanism. A thermodynamic and kinetic study revealed that the monolayer adsorption occurred and was dominated by chemisorption. Density functional theory (DFT) and frontier orbital theory (FOT) simulations were conducted to further explore the interfacial interaction micro-mechanism at the molecular and electronic levels. The adsorption equilibrium configurations confirmed that SMT was adsorbed onto MCB in the V-shape configuration, mainly through π-π EDA interactions. DFT simulations showed that increasing the π electron density of the biochar favored its adsorption of SMT and that the pyrrole groups might be the most effective functionalities for this adsorption. The above findings could provide significant reference value for the design and preparation of efficient sulfonamide antibiotic biochar adsorbents.

* Corresponding author.
E-mail address: celjzh@scut.edu.cn (L. Zhang).

https://doi.org/10.1016/j.cej.2018.09.055
Received 29 June 2018; Received in revised form 17 August 2018; Accepted 7 September 2018
Available online 08 September 2018
1385-8947/

1. Introduction

Sulfamethazine (SMT) is a broad-spectrum sulfa-antibiotic that has been employed in aquaculture and livestock feed due to its simplicity usage, high chemical stability, broad-spectrum antimicrobial activity, fast absorption and low price [1]. However, its unreasonable use leads to excessive residue in environmental media such as farmland soil, living organisms and water [2]. Consequently, the residual SMT may inhibit the growth of micro-organisms and damage the ecosystem balance. Moreover, SMT may prompt the formation of antibiotic genes, which could enter the human body through the food chain and thus endanger health [3,4]. A series of methods has been practiced for removing SMT, including catalytic degradation, membrane separation, and biological and chemical adsorption [5–10]. Among these processes, adsorption is mostly valued for its simple operating procedures, low cost and high safety [11,12]. Nonetheless, the adsorption efficiency is mainly related to the structures of the adsorbents and adsorbates and other environmental factors [13,14].

Biochar has high carbon content, large surface area, good adsorption performance, and economic advantages and has thus been most frequently employed as a new type of environmental functional material [15,16]. Using biochar as an adsorbent can not only effectively remove pollutants but also achieve the rational use of natural resources [17]. However, determining how to design and prepare efficient biochar adsorbents remains a challenge. Cellulose is the main component of agricultural waste, and its content in wheat straw, corn straw, and rice straw is 33–40%, approximately 45% and approximately 40%, respectively [18]. Hence, using cellulose as a raw material to prepare biochar adsorbent is an effective approach to eliminate SMT.

Previously, much work has focused on SMT removal using biochar adsorbents. F. Wang et al. prepared straw biochar pyrolyzed at 300 °C (BC300) and 600 °C (BC600) for SMT removal. Physisorption and weak chemical binding (π-π electron donor-acceptor (EDA) interactions) dominated the adsorption of SMT onto BC300 and BC600, respectively [19]. Y.S. Ok's group developed a series of biochar preparation technologies and produced several biochar adsorbents that were derived from tea waste and the invasive plant *Sicyos angulatus* L. They investigated the SMT removal performance and discussed the adsorption mechanism through theoretical models, finding that physical adsorption, electrostatic interactions and π-π EDA interactions were the main interaction mechanisms [20,21]. Surprisingly, most of the efforts focused on the adsorbent preparation procedure, the selection of raw materials, the evaluation of adsorption performance, the factors that affect the adsorption performance, and the prediction of the adsorption mechanism through theoretical models. Nevertheless, they were rarely systematic concerning the microscopic mechanism (micro-mechanism) of interfacial interaction, especially at the molecular and electronic levels. There is thereby an urgent need to explore the adsorption micro-mechanism, which is of great significance in guiding the preparation of efficient biochar sulfonamide antibiotic adsorbents and thus improving the removal efficiency. Meanwhile, understanding the micro-mechanism only through experiments is difficult, and computer simulations realize it.

Density functional theory (DFT) is a fundamental theory of electronic structure and generally accepted to enable the further exploration of the adsorption micro-mechanism [22]. X.K. Wang et al. revealed the π-π stacking effect between reduced graphene oxides and endocrine-disrupting chemicals and explained the strong binding energy of interactions between adsorbates and adsorbents through DFT calculations [23]. Yu's group discussed the micro-mechanism of perfluorooctanoate (PFOA) adsorption onto MIL-101 (Cr) metal-organic frameworks (MOFs) by a comparison of DFT calculations and sorption experiments, and the results revealed that the major adsorption mechanism was a combination of Lewis acid/base complexation, anion exchange and electrostatic interactions [24].

Taking the above factors into consideration, we herein use mesoporous cellulose biochar (MCB) produced with different carbonization times as adsorbents and SMT as the adsorbate to explore the influences of pH value, cations and humic acid (HA) on the interfacial interaction. Classical adsorption theory models are used to analyze the adsorption process, interfacial phenomena and kinetic behavior and to predict the interfacial interaction mechanism of adsorption. Moreover, the adsorption micro-mechanism will be deeply explored by DFT/frontier orbital theory (FOT) simulations, especially at the molecular and electronic levels. The objective of this work is to clarify the interfacial interaction mechanism of sulfonamide antibiotic adsorption onto biochar, and to provide theoretical guidance for the design and preparation of efficient biochar adsorbents.

2. Materials and methods

2.1. Materials

Mesoporous cellulose biochar (MCB) adsorbents were prepared through a 300 °C carbonization-KOH activation-700 °C carbonization-HNO_3 oxidation process with cellulose (α-Cellulose, Powder, Sigma) as raw material, and the typical preparation process and structural characterization were shown in our another work [25]. Briefly, a clear internal layer, a large number of nanoscale pores and channels were observed in the SEM images, the BET determined surface area, pore volume and pore sizes were about 550–600 m^2/g, 0.35 cm^3/g and 3.2 nm. The functional groups of the MCB were measured by FTIR and XPS, the related functional groups content of MCB-1h–3h (1 h, 2 h and 3 h refer to carbonization times of 1, 2, and 3 h at 700 °C) are listed in Table 1.

A primary SMT stock solution of 100 mg/L was prepared with 1% methanol and stored at 4 °C. An HA stock solution was prepared by dissolving HA powder (96%, J&K) in ultrapure water at pH 11.0 (adjusted by 5.0 mM NaOH solution), which was then filtered through a 0.45 μm filter membrane and adjusted to pH 7.0 with a 5.0 mM HCl solution, and the concentration of the HA stock solution was determined using a TOC analyzer (TOC-Vcph, Shimadzu). Methanol, formic acid and acetonitrile (high-performance liquid chromatography (HPLC) grade, J&K), cadmium chloride hemi (pentahydrate) ($CdCl_2{\cdot}2.5H_2O$, 99%, J&K), copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$, 99%, J&K), potassium chloride, sodium chloride and nitric acid (KCl, NaCl and HNO_3, respectively, AR, Guangzhou Chemical Reagent Factory), calcium chloride, acetic acid, sodium hydroxide and hydrochloric acid ($CaCl_2$, CH_3COOH, NaOH and HCl, respectively, AR, Sinopharm Group) were used directly.

Table 1
The relative functional group content and BET data of MCB-1h–3h.

Matrix	OH−	COOH−	NO_2−	NH_2−	C_5H_5N−	C_4H_5N−	BET surface	Pore volume	Pore size
MCB-1 h	21.1	5.3	4.2	20.0	5.1	19.1	597.7	0.36	3.23
MCB-2 h	11.5	3.1	22.1	13.1	11.1	10.3	563.8	0.34	3.13
MCB-3 h	17.3	3.2	16.3	7.6	13.3	12.4	557.1	0.33	3.19

Notes: BET surface (m^2/g); pore volume (cm^3/g); pore size (nm).