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Adsorption of tetracycline and chloramphenicol in aqueous solutions by bamboo charcoal: A batch and fixed-bed column study

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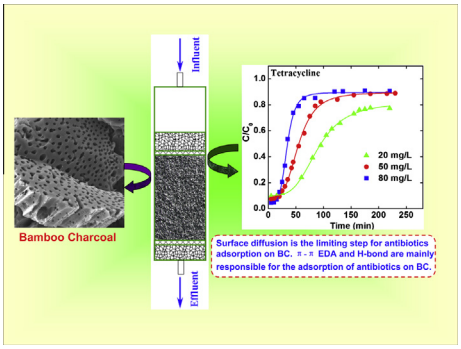
HIGHLIGHTS

- A new porous carbonaceous adsorbent was investigated for antibiotics adsorption.
- Bamboo charcoal (BC) exhibits a strong adsorption affinity to antibiotics.
- The key process controlling the rate of antibiotics adsorption was identified.
- The mechanism regarding BC adsorption of antibiotics was explored.
- BC could be used as a potential adsorbent for antibiotics removal in wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption of two antibiotics, tetracycline (TC) and chloramphenicol (CAP), on a new porous carbonaceous adsorbent, bamboo charcoal (BC), is investigated in batch and fixed bed column experiments. Adsorption isotherms of TC and CAP obtained from batch experiments are better fitted by Freundlich and Dubinin–Radushkevich models compared with Langmuir model. In the fixed bed column experiments, lower bed height, higher flow rate and lower influent contaminant concentration lead to greater adsorption of TC and CAP on BC. A mass transfer model that incorporates both surface and intraparticle diffusion theory into the convection–dispersion equation (CDE) is developed to identify the key process controlling the rate of TC and CAP adsorption. The results demonstrate that the surface diffusion is the rate-limiting step for antibiotics adsorption onto BC, which is consistent with the results of traditional Adams–Bohart model. π–π Electro-donor–acceptor (EDA), cation-π bond in conjunction with hydrogen bonding interaction are the main mechanisms for the adsorption of TC and CAP on BC, while the hydrophobic interaction and electrostatic interaction have minor contributions.

1. Introduction

Pharmaceutical antibiotics including tetracycline (TC) and chloramphenicol (CAP) are produced in large quantities and are commonly used to treat the diseases caused by microorganisms [1,2]. The occurrence and fate of antibiotics in the environment is recognized as one of the emerging issues in environmental chemistry [3]. Owing to their antibacterial nature which prevents effective removal in traditional wastewater treatment plants [4], they have been frequently detected in surface water, groundwater,

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and even drinking water [5]. Easy access to low-level antibiotics in the aquatic environment has raised significant concerns of the toxic effect and the transfer and spread of antibiotics resistant genes in microorganisms [6]. It is therefore of great importance to develop an efficient and cost-effective strategy for removal of antibiotics in contaminated waters.

Adsorption by porous materials is effective in removing antibiotics from aqueous solution because of its low energy cost, high adsorption capacity as well as environmental friendliness [7–10]. Engineered activated carbon (AC) and carbon nanotubes (CNTs) have been used in water purification [11,12]. Unfortunately, AC has the shortcomings of slow desorption kinetics and difficulties in regeneration, which arises primarily from the closed, irregular-shaped, and highly porous micropores with wide pore size distribution [13]. CNTs are relatively costly ($120–180 per kilogram) and have potential toxicity [14]. As a promising porous carbonaceous adsorbent, bamboo charcoal (BC) has demonstrated an extraordinary adsorption capacity for removing many organics and heavy metals due to its large surface area and pore volume as well as high hydrophobicity [10,15–19]. BC can be produced from moso bamboo plants which are widespread in China, grow fast, and have a short growth period [18]. Bamboo is considered as an alternative to wood in the 21st century. The total species, growing stock and harvesting amount of moso bamboo in China are the greatest in the Asia–Pacific region [18]. Despite of the potential importance, limited attention has been paid to adsorption of antibiotics on BC. Fan et al. [10] preliminarily investigated the adsorption of CAP on NaOH modified BC in a batch mode, but the underlying mechanism controlling adsorption is still largely unknown.

Previous investigations have examined antibiotics adsorption on different environmental matrices, including soils, iron/aluminum hydroxides, clay minerals, humic substances, and CNTs [8,9,20–22]. It is proposed that the adsorption is mainly controlled by cation/anion exchange, cation bridging, π–π electro-donor–acceptor (EDA), and surface complexation (e.g., H-bonding) between the functional groups of antibiotics and the charged/polar sites of adsorbents [9,22]. However, the properties of BC are significantly different from the aforementioned materials, suggesting the different adsorption mechanism. Our recent results revealed that four interactions, including van der Waals forces, hydrophobic effect, electrostatic interaction, and π–π EDA interaction, were responsible for the adsorption of dyes and nitrogen-heterocyclic compounds (NHCs) on BC [15–17]. Nonetheless, the molecule structures of antibiotics are noticeably distinct with dyes and NHCs. Consequently, it is crucial to elucidate the mechanism of antibiotics adsorption on BC.

The continuous fixed bed adsorption process approximates the practical application of BC adsorption, which provides a better understanding of the adsorption mechanism [15]. It is well-documented that the adsorption of antibiotics on adsorbents in a fixed bed column involves the following three steps: (i) antibiotics molecules diffuse from the liquid phase to the liquid–solid interface; (ii) antibiotics molecules move from the liquid–solid interface to the solid surface; and (iii) antibiotics molecules diffuse into the particle pores [23]. To reveal the relative contribution of surface and intraparticle diffusion for the fixed bed adsorption process, several mass transfer models such as surface diffusion model (SDM) [24], pore diffusion model (PDM) [25], and bed depth service time (BDST) model [26] have been developed. Nevertheless, these models either overestimate the importance of individual contribution or only emphasize on the bed parameters, making it difficult to quantitatively measure their relative contributions [27]. As a result, a new quantitative mass transport model that combines both surface and intraparticle diffusion parameters can be more robust for measuring the relative contribution of each interaction.

In this study, adsorption of two commonly antibiotics, TC and CAP, on BC in batch and fixed bed column is investigated. The main objectives are (1) to evaluate the performance of BC in antibiotics adsorption in a batch mode; (2) to investigate the effect of various operating variables as fixed bed, flow rate, and influent concentration on antibiotics adsorption in the column; (3) to develop a new quantitative mass transport model to identify the key process controlling the rate of antibiotics adsorption on BC in the column; and (4) to provide the direct evidence regarding the relative importance of multiple mechanisms for adsorption of antibiotics on BC.

2. Materials and methods

2.1. Chemicals and materials

TC (⩾98%) was purchased from Sigma–Aldrich (Madrid, Spain) and CAP (⩾98%) was supplied by Acros Organics (Geel, Belgium). The properties of TC and CAP are listed in Table 1. The procedure for BC production was similar to our previous work with the exception of production temperature [16]. Briefly, certain amounts of 4-year-old moso bamboo (*Phyllostachys pubescens*) were cut into different sections and were evaporated at 100–150 °C for 2–3 d, pre-carbonized at 150–250 °C for 1–2 d, carbonized at 250–400 °C for 0.5–1 d, calcined at 400–700 °C for 0.5–1 d, and finally kept at 700 °C for a short time. Our preliminary experiments demonstrated that these operating conditions could reach the maximum mass of BC production with minimum energy consumption. All the processes were carried out in a kiln burner under nitrogen atmosphere. The obtained massive BC was ground and sieved through a 60-mesh screen. After washed with DI water, the BC particles were dried at 105 °C for 6 h and stored for use. The main characteristics of BC are summarized in Table 2, showing the predominant existence of mesopores (2–50 nm) and the main elements of carbon, oxygen, hydrogen and nitrogen. The surface area of BC is much larger than that reported in literatures [10], probably due to the much higher production temperature (≈700 °C). The structure of BC primarily consists of graphite sheets rimmed with functional groups (i.e., C—C, C—O, C═O, COO—, π–π*, C═N) on the edge forming connected mesoporous network [10,15–18]. The surface of BC is negatively charged at the pH of 7.0. DI water (18.0 MΩ cm) was obtained from a Millipore Milli-Q system. All the other reagents were above analytical grade.

2.2. Procedures and equipments

2.2.1. Batch experiments

The adsorption was first carried out in a batch mode at 303 ± 1 K. For the adsorption kinetics, a weighed quantity of BC (0.02 g) and 20 mL of aqueous solution containing 30 mg/L TC or CAP were added into a 30-mL serum bottle. Preliminary experiments showed that adsorption at this dosage gave a straightforward comparison of adsorption data. All adsorption experiments were obtained in 0.01 mol/L $CaCl_2$ to simulate environmental water, with 200 mg/L NaN_3 added to inhibit the degradation by incidental bacteria. The bottles were sealed and placed in a shaking table at 150 rpm in dark. At regular time intervals (0, 1, 3, 5, 7, 9, 12, 16, 18, and 24 h), the bottles were taken out for antibiotics analysis. With respect to adsorption isotherms, the equilibrium time was set at 24 h with different initial antibiotics concentrations (5–100 mg/L). The initial pH was set at 7.0 and the variation was less than 0.2 during the whole process. Control experiments