JOURNAL OF ENVIRONMENTAL SCIENCES XX (2018) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Study of ciprofloxacin removal by biochar obtained from used tea leaves

Jie Li[1,2], Guangwei Yu[1,*], Lanjia Pan[1,2], Chunxing Li[1], Futian You[1], Shengyu Xie[1,2], Yin Wang[1,*], Jianli Ma[3], Xiaofu Shang[3]

1. Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China. E-mail: jieli@iue.ac.cn
2. University of Chinese Academy of Sciences, Beijing 100049, China
3. Tianjin Huankelijia Environment Remediation Technology Co., Ltd., Tianjin 300191, China

ARTICLE INFO

Article history:
Received 21 September 2017
Revised 22 December 2017
Accepted 28 December 2017
Available online xxxx

Keywords:
Biochar
Used tea leaves
Ciprofloxacin adsorption
Isotherm
Kinetics
Mechanism

ABSTRACT

In this study, used tea leaves (UTLs) were pyrolyzed to obtain used tea-leaf biochar (UTC), and then the UTC was used as an adsorbent to remove ciprofloxacin (CIP) from aqueous solutions. Batch experiments were conducted to investigate the CIP adsorption performance and mechanism. The results showed that the CIP-adsorbing ability first increased and then declined as the UTC pyrolysis temperature increased. The UTC obtained at 450°C presented excellent CIP-absorbing ability at pH 6 and 40°C. The maximum monolayer adsorption capacity was 238.10 mg/g based on the Langmuir isotherm model. The pseudo-second-order kinetic equation agreed well with the CIP adsorption process, which was controlled by both external boundary layer diffusion and intra-particle diffusion. The characterization analysis revealed that the –OH groups, C=C bonds of aromatic rings, C–H groups in aromatic rings and phenolic C–O bonds play vital roles in the CIP adsorption process, and that the N–C, N–O, O–C=O and C–OH groups of UTC were consumed in large quantities. π–π interactions, hydrogen bonding and electrostatic attraction are inferred as the main adsorption mechanisms. The present work provides not only a feasible and promising approach for UTL utilization but also a potential adsorbent material for removing high concentrations of CIP from aqueous solutions.

Introduction

Tea leaves are extensively used to provide flavor in beverages. In China, 20% of the domestic beverage market is occupied by the tea beverage industry. It was reported that the output of tea leaves was 2.27 million tons in 2015, and more than 2 million tons of used tea leaves (UTLs) were left after consumption (Shen et al., 2017). The accumulation of UTL on the ground is a burden to the ecological environment and causes a vast waste of resources (Zhu et al., 2013). Thus, finding an appropriate disposal method for UTL is extremely urgent. The traditional approach to UTL treatment is to burn it for thermal energy. However, incineration contributes to environmental pollution, such as greenhouse gases and other forms of air pollution (Bartolozzi et al., 2017).

In addition, ciprofloxacin (CIP), as a third generation fluoroquinolone antibiotic, has become one of the most commonly detected antimicrobial agents due to its widespread application for decades in China (Wang et al., 2016). It has been frequently detected in the excrement of livestock and in soil and water

* Corresponding authors. E-mails: gwyu@iue.ac.cn (Guangwei Yu), yinwang@iue.ac.cn (Yin Wang).

https://doi.org/10.1016/j.jes.2017.12.024
1001-0742/

Please cite this article as: Li, J., et al., Study of ciprofloxacin removal by biochar obtained from used tea leaves, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2017.12.024

because of its high stability and bacteria-inhibiting effects (Mao et al., 2016). It has been reported that the CIP concentration in wastewater is as high as 31 mg/L, with higher concentrations in the effluents from drug production plants (Zhang et al., 2017). CIP has been proven to be an emerging genotoxic contaminant that can damage ecosystems and human health *via* its acute and chronic toxicity (Espinosa et al., 2015; Li et al., 2014). Therefore, the removal of CIP from aqueous environments has become an urgent issue. Many approaches have been developed to treat CIP in contaminated water, such as biological, photolytic/photocatalytic, oxidation and adsorption treatments (Diao et al., 2017; Liao et al., 2016; Tu et al., 2014). Among these methods, adsorption technology is considered to be a promising approach based on its simple design, easy operation, relatively simple maintenance and environmental friendliness (Alahabadi et al., 2007).

In recent years, many works have been undertaken to develop alternative and more economical adsorbents. As raw material for adsorbents, biomass-like waste byproducts from large-scale industrial operations and agricultural adsorbents have attracted the interest of investigators (Alahabadi and Moussavi, 2017; Fernandez et al., 2015). Regarding UTL, some new treatments have been provided to preferably utilize UTL with higher added value, including its direct use as an adsorbing material and its use as a raw material to prepare active carbon and biochar (X. Li et al., 2015b; Peng et al., 2013). Among the above approaches, producing biochar by pyrolysis as an adsorbent to remove organic contaminants is a promising choice. Recently, some works have studied the adsorption of organic pollutants, such as carbofuran and sulfamethazine, by biochar derived from UTL (Vithanage et al., 2016; Rajapaksha et al., 2014). However, little work has been done to investigate the effect of biochar obtained from used tea leaves on the adsorption of ciprofloxacin.

In this study, UTL was pyrolyzed to produce used tea-leaf biochar (UTC), and then the UTC was used to adsorb CIP. The effects of various operating parameters, including the UTC pyrolysis temperature, contact time, CIP concentration, solution temperature and pH, were investigated in detail. Moreover, the adsorption kinetics and isotherms were studied, and the adsorption mechanism was deduced based on the analysis of the characteristics of UTC before and after CIP adsorption.

1. Materials and methods

1.1. Raw materials and preparation of UTC

Ciprofloxacin (CIP), analytical standard grade, was purchased from the Aladdin Industrial Corporation in Shanghai, China. All other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. and were of analytical grade. CIP solutions were prepared at various initial concentrations for the batch adsorption experiments, and Milli-Q water was used in all experimental procedures.

The used tea leaves (UTL) were collected from Fujian Xian Yang Yang Food & Technology Co., Ltd., Ningde City of Fujian province, China. The UTL were ground and sieved through a 100-mesh sieve after drying and then stored in a clean airtight container. Detailed information about UTL was obtained via proximate and ultimate analysis. The dry-based contents of ash, volatiles and fixed carbon in UTL were 4.88, 72.98 and 22.14 wt.%, respectively, and the base dry-ash-free contents of H, C, N, O and S were as follows: 4.46, 48.05, 3.12, 43.74 and 0.63 wt.%, respectively.

The UTL was pyrolyzed at five different pyrolysis temperatures (350, 400, 450, 500 and 550°C) for 30 min with a ramp rate of 10°C/min in a vertical tubular furnace under nitrogen atmosphere (Fig. 1). The solid pyrolysis product, UTC, was ground after cooling down and then screened through a 200-mesh sieve; subsequently, the samples were stored in clean airtight containers until they were used for subsequent experiments.

1.2. Adsorption tests and detection of CIP

1.2.1. Adsorption tests of CIP

Batch adsorption experiments were conducted by adding 0.2 g of UTC to 150 mL of the CIP solution in sealed conical flasks. The sealed conical flasks were placed in a temperature-controlled light-protected shaker at a speed of 200 r/min for 24 hr. The samples collected during the batch adsorption experiments were filtered through a 0.45 μm membrane before detection. All the measurements were repeated three times, and the error was calculated to support the data accuracy.

The effects of the experimental conditions on CIP adsorption were investigated as follows.

(1) Six different initial concentrations (150, 200, 250, 300, 400 and 500 mg/L) were selected to study the effect of the CIP concentration. The pH and temperature of the CIP solutions were 6 and 30°C, respectively.
(2) To investigate the effect of the contact time, samples were withdrawn at different time intervals during the 24 hr period. The adsorption experiments were conducted at pH 6 and 30°C for CIP solutions at three different concentrations (150, 200 and 250 mg/L).
(3) The effects of the solution temperature on absorption were studied at 30, 35, 40, 50 and 60°C at pH 6 and with an initial CIP concentration of 200 mg/L.
(4) The effects of pH on the CIP adsorption were determined using samples with an initial CIP concentration of 200 mg/L at 30°C. The pH of the sample solutions was adjusted to different values (4, 5, 6, 7, 8 and 10) using 0.1 mol/L NaOH or 0.1 mol/L HCl.

1.2.2. Models of the adsorption kinetics and isotherms

The pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model (Nasuha et al., 2010) were selected to determine the adsorption kinetics of CIP by UTC based on the experimental adsorption data from various contact times.

To identify the adsorption behavior of the CIP molecules with UTC, the equilibrium isotherm data at six different initial CIP concentrations were modeled using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm equations individually (Fan et al., 2016).

1.2.3. Detection of CIP

The CIP concentration in the filtrate was detected with high-performance liquid chromatography (HPLC, L-2000, Hitachi, Japan) at a column temperature of 30°C and wavelength of

Please cite this article as: Li, J., et al., Study of ciprofloxacin removal by biochar obtained from used tea leaves, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2017.12.024