Process Safety and Environmental Protection xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Removal of cephalexin from effluent by activated carbon prepared from alligator weed: Kinetics, isotherms, and thermodynamic analyses

Ming-Sheng Miao[a], *Qun Liu*[a,b], *Li Shu*[c], *Zhen Wang*[a], *Yu-Zhen Liu*[b], *Qiang Kong*[a,b,*]

[a] *College of Life Science, Shandong Normal University, 88 Wenhua Donglu, Jinan 250014, Shandong, PR China*
[b] *College of Geography and Environment, Shandong Normal University, 88 Wenhua Donglu, Jinan 250014, Shandong, PR China*
[c] *School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne, Australia*

ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form 20 March 2016
Accepted 24 March 2016
Available online xxx

Keywords:
Alligator weed
Activated carbon
Cephalexin
Adsorption

ABSTRACT

Low-cost activated carbon was produced from alligator weed by phosphoric acid activation. The cost of production of alligator weed-activated carbon (AWAC) was CN¥ 2.1/kg and the content of activated carbon (AC) in AWAC was 35.33%. AWAC was used as an adsorbent to adsorb cephalexin (CEX) from aqueous solution. Scanning electron microscopy (SEM) analysis of AWAC revealed a highly porous structure with a rough surface. AWAC featured a high surface area of 736.3 m^2/g and an average pore size of 4.05 nm, which were responsible for its excellent adsorption ability. The maximum CEX adsorption capacity of AWAC was ∼45 mg/g. The Langmuir isotherm ($R^2 = 0.9967$) gave the best correlation with the experimental data at 308 K, indicating monolayer adsorption. The kinetic model data on AWAC fit well to the pseudo-second-order kinetic equation, which is considered as the rate-limiting factor. Fourier transform infrared spectroscopy analysis revealed the presence of phosphorus-containing groups and C–H, C–O, and C=C moieties on the surface of AWAC. Following adsorption, the intensity of the spectral peaks of AWAC decreased owing to coverage of the CEX species or reaction with the functional groups of CEX.

1. Introduction

With the development of the economy and society, antibiotics are being increasingly applied in the pharmaceutical industry, stock farming, and bio-manufacturing. Such widespread use results in the discharge of large quantities of antibiotics in the aquatic life and industrial sewage. However, around 30–90% of currently available antibiotics is not completely metabolized in the organism and is excreted through urine and feces, which are subsequently discharged into the environment as active compound (Wollenberger et al., 2000). Recent studies have shown that numerous antibiotics are toxic to algae and other lower organisms, thereby posing a threat to ecological sustainability. Therefore, adopting efficient measures to address water body pollution by antibiotics discharge is essential.

More specifically, cephalexin (CEX), a type of semi-synthetic cephalosporin antibiotic, is widely employed for treating infections in human or animal bodies owing to its broad antibacterial activity (Watkinson et al., 2007). It is also commonly employed for aquatic products, agricultural products, and livestock breeding. A mass of CEX is immediately discharged into the liquid solutions without being utilized by organisms. CEX in water accumulated to a certain amount may interfere the physiological functions of humans and

---

[*] Corresponding author. Tel.: +86 531 86182550; fax: +86 531 86180107.
E-mail address: kongqiang0531@hotmail.com (Q. Kong).

http://dx.doi.org/10.1016/j.psep.2016.03.017
0957-5820/

Please cite this article in press as: Miao, M.-S., et al., Removal of cephalexin from effluent by activated carbon prepared from alligator weed: Kinetics, isotherms, and thermodynamic analyses. Process Safety and Environmental Protection (2016), http://dx.doi.org/10.1016/j.psep.2016.03.017

animals body by mutagenic and carcinogenic effects (Kong et al., 2016). CEX is also highly resistant to degradation, thereby remaining active and industrial route within excretion. Thus, the long-term presence of CEX in the environment can cause health problems in the near future.

The removal of CEX residues from effluents is therefore important and has generated much research interest. Numerous methods have been employed for the removal of antibiotics as adsorbents that involve the use of non-ionic polymeric resins, activated carbon, ion-exchange resins, and oxidized celluloses (Dutta et al., 1999). Biosorption has generated the most interest toward the removal of CEX from liquid solutions as it employs dead biomass as adsorbent. Adsorption is the most effective and versatile method for removing pollutants like mental ions and antibiotics, especially, if united with suitable regeneration process (Bailey et al., 1999). Additionally, activated carbon has been widely used to remove harmful substances from water and wastewater owing to its low cost, high surface area, well-developed adsorption porosity, and simplicity of the technology. However, at present, there are only few papers reporting on the removal of CEX by activated carbon; moreover, the associated sorption mechanisms have yet to be more comprehensively examined (Dutta et al., 1997).

Alligator weed is a South American algae species that has spread on all continents except Africa and Europe. In Australia, it grows in both aquatic and terrestrial habitats and is considered a fearful potential threat (Julien et al., 1995), whereas in China, it can be found in provinces south of the Yangtze River. However, alligator weed has reached its limits of spread in the USA and China, while expanding its distribution in Australia. Thus, alligator weed is considered a problematic weed in many countries, and several measures have been taken to control and manage the spread of alligator weed. However, alligator weed can produce large amounts of biomass, which can be used as a raw material to prepare high-efficiency activated carbon. To our knowledge, there are no studies on the use of alligator weed-activated carbon (AWAC) as an adsorbent for the removal of antibiotic in effluents.

Accordingly, the current study aims to develop a highly effective method for preparing activated carbon from alligator weed and to study its suitability to absorb antibiotic CEX in solutions. Langmuir, Freundlich, and Dubinin–Radushkevich models were then employed to correlate the experiment data on which equations equally well fit the data. For kinetic data, pseudo-first-order, pseudo-second-order, and particle diffusion model are selected. The adsorptive mechanisms were investigated through scanning electron microscopy (SEM), pore-size distribution, Brunauer–Emmett–Teller (BET), and Fourier transform infrared (FTIR) spectroscopy analyses. The adsorption performance of AWAC was examined by assessing the effects of various parameters, i.e. initial CEX solution concentration, contact time, adsorbent dosage, temperature, and pH on the adsorption properties of AWAC.

2. Materials and methods

2.1. *Materials and chemicals*

Alligator weed that was used for preparing the activated carbon examined in this paper was collected from Xiaoqing River in Shandong Province, China. Alligator weed was first sectioned into 2–3 cm in length, washed with distilled water to remove surface-attached ash or wax, and then dried at 105 °C in oven for 24 h. The sample was then soaked in 2 wt% NaOH for 24 h at room temperature. Then the sample was washed with distilled water until a constant solution pH of ~7 was achieved and dried overnight at 105 °C and then dried at 200 °C for 1 h. After drying, the resulting precursor material was immersed in 85 wt% phosphoric acid solution at a precursor/phosphoric acid solution ratio of 1:4 (w/w) for 6 h at room temperature. The resulting sample was then carbonized in muffle furnace (Yong Guangming Company, Beijing) at 600 °C for 1 h. The resulting activated carbon was then cooled to room temperature, washed repeatedly with distilled water until the pH of the filtrate was 6–7, and then dried at 105 °C for 12 h in a vacuum oven. Finally, the activated carbon was ground into powder prior to conducting the adsorption tests (Fan et al., 2011).

The CEX (CB0280) was supplied by Life Science Products & Science (China) and used as-received. The molecular weight of CEX is 347.39 g/mol and it has a chemical formula of $C_{16}H_{17}N_3O_4S$; CEX solution used was 35 mg/L (0.035 g of CEX was accurately weighed and dissolved in 1000 ml of distilled water). Other chemicals used in this study were of analytical level. Distilled water was used throughout for solution preparations. The pH of the solutions was adjusted with acid and alkali.

2.2. *Calculation of AWAC content*

The AWAC ratio (Y, wt%) content reflects the quality of activated carbon in AWAC defined as follows:

$$Y = \frac{m_1}{m_2} \times 100, \quad (1)$$

where m_1 is the mass of the obtained activated carbon and m_2 is the mass of the dry raw material alligator weed.

2.3. *Characterization of AWAC*

The specific surface area of an adsorbent is an important factor that influences the adsorption efficiency. The Brunauer–Emmett–Teller (BET) surface area was obtained from nitrogen adsorption–desorption isotherms measured at 77 K using an automated surface area analyzer (Quantachrome, USA). The determination of the pore size distribution was detected using medium regularization by density functional theory (DFT). The surface structural characteristics of AWAC were observed via scanning electron microscopy (SEM) (SUPRA^{TM} 55, Zeiss Company, Germany). Infrared spectra were recorded on a Fourier transform infrared (Thermo Scientific, USA) spectrometer to examine the chemical functional groups present on the studied materials. The spectra were recorded in the wavenumber range of 400–4000 cm^{-1} (Wang et al., 2011).

2.4. *Batch adsorption experiments*

Batch adsorption experiments were devoted to study the influence of initial concentration of CEX, adsorbent dose of AWAC, solution pH, contact time, and temperature of reaction on the adsorption uptake (Fan et al., 2011). Prior to the batch adsorption experiments, CEX solutions of varying concentrations were prepared by dilution with distilled water. A standard curve was constructed by measuring the absorbance of the different CEX solutions on a UV–visible spectrophotometer (T6-Xinshiji, Beijing) at a maximum wavelength of 262 nm.

Please cite this article in press as: Miao, M.-S., et al., Removal of cephalexin from effluent by activated carbon prepared from alligator weed: Kinetics, isotherms, and thermodynamic analyses. Process Safety and Environmental Protection (2016), http://dx.doi.org/10.1016/j.psep.2016.03.017