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Tetracycline adsorption by H_3PO_4-activated carbon produced from apricot nut shells: A batch study

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ABSTRACT

Tetracycline (TC) batch adsorption was investigated in a synthesized aqueous solution using activated carbon (AC) prepared from apricot shell. The adsorbent was produced via a chemical activation method using phosphoric acid. The specific surface area, total pore volume, and average pore diameter were 307.6 $m^2\,g^{-1}$, 0.191 $cm^3\,g^{-1}$, and 1.957 nm, respectively. Our analysis revealed that the material produced primarily consisted of mesopores (61.1%). The effect of adsorbent dosage, contact time, initial TC concentration, temperature, and initial pH of the solution on TC adsorption was studied. A thermodynamics analysis revealed that the adsorption process is endothermic and spontaneous. Adsorption isotherms were investigated, and it was shown that the Freundlich model was the best fit for the adsorption equilibrium data. The maximum adsorption capacity of TC onto activated carbon was 308.33 $mg\,g^{-1}$, and the adsorption kinetics perfectly matched those of the pseudo-second order model. It was concluded that adsorption of TC is controlled by both intra-particle diffusion and film diffusion mechanisms. The results showed the successful application of synthesized activated carbon for effective removal of TC.

1. Introduction

Tetracycline (TC) is a broad spectrum antibiotic and its low cost, high quality, and appropriate antimicrobial properties have meant that it has become one of the most widely used antibiotics, worldwide (Saitoh et al., 2014). In the USA and Europe, approximately 5500 tons of TC are annually consumed, and statistics show that 90% of ingested TC agents are discharged as surface water in the form of urine (D. Zhang et al., 2015), (Martins et al., 2015). Improper disposal of expired medicines is also considered to be another important source by which antibiotics enter surface water and ground water (Zhu et al., 2014). The most important risk resulting from the presence of TC in surface water is increased resistance of bacterial strains, and these developed strains cannot usually be removed using conventional wastewater treatment. When these strains subsequently enter a host's body, they can cause illnesses that cannot be treated using established therapies (Zhu et al., 2013). TC has been detected in surface water at concentrations in the range of 0.11–4.20 $\mu g\,L^{-1}$ (Ocampo-Pérez et al., 2012). In order to solve this problem, a variety of technically or economically unsuitable methods for the treatment of pharmaceutical wastewater have been proposed. For example adsorption process often demands high investment expenditures; Coagulation and flocculation methods produce a large amount of sludge; chemical oxidation

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method requires expensive reactants as well as transmission and storage of hazardous chemicals. Most recent works in this field are TC removal by degradation and flocculation with nanoscale zerovalent iron (Fu et al., 2015), photo degradation by surfactant-assisted coagulation – sedimentation method (Saitoh et al., 2014) and TC degradation by highly porous MnO_2 nanosheet assembly (Mahamallik et al., 2015).

The advantages of adsorption over other processes are non-toxic by-products and high removing percentage of undesirable dissolved compound from solution (Rivera-utrilla et al., 2013b) and therefore this process was selected to be the focus of this study.

It has previously been extensively reported that different forms of adsorbent material, synthetic, mineral, and biological, remove TC from wastewater. The low-cost adsorbent that is produced by raw materials, such as agricultural waste, makes adsorption an operational process. Recent studies of producing adsorbent are sludge-derived adsorbents (Ocampo-Pérez et al., 2012; Rivera-utrilla et al., 2013a), porous carbon from waste hydro char (Zhu et al., 2014), petroleum coke-derived highly porous activated carbon (D. Zhang et al., 2015), Fe–Mn binary oxide (Liu et al., 2012), amino-Fe (III) functionalized SBA15 (Z. Zhang et al., 2015), sponge like RCGEM, polyacrylamide cryogels (Ers, 2013) and activated carbon produced from agricultural waste like bamboo charcoal (Liao et al., 2013), macadamia nut shells (Martins et al., 2015) and vine wood (Pouretedal and Sadegh, 2014). In this study, activated carbon was synthesized using hard shell of apricot stone as precursor which was used for TC batch adsorption in aqueous solution. This work evaluates adsorption characteristics of TC onto produced activated carbon by investigating the effect of experimental parameters such as adsorbent dosage, contact time, solution initial pH, initial TC concentration and temperature. Maximum removal of TC from solution was achieved by applying the optimized amount of mentioned parameters. The thermodynamics, kinetics and equilibrium studies were also conducted for better understanding of adsorption process.

2. Materials and methods

2.1. Materials

TC hydrochloride salt with a purity of 99.1% was obtained from the Sinadaro Pharmaceutics Company (Tehran, Iran). The hard shell of apricot stone was chosen as raw material for producing activated carbon. It has a 50.5% weight carbon and its structure also contains 39.75% cellulose and 34.50% lignin. Phosphoric acid (H_3PO_4) with a purity of 85% was used as an activation agent for the synthesis of activated carbon and was supplied by the Merck Company.

2.2. Adsorbent preparation and characterization

First, the apricot shell (AS) was washed with hot distilled water to remove impurities, and it was then ground using a sieve-shaker. The pieces were categorized on the basis of size, and particles of approximately 500 nm were selected for study. Phosphoric acid was added to AS at a 1:1 impregnation weight ratio. The mixture was heated in an air oven at 100 °C for 24 h. For carbonization and activation, the heated mixture was placed in an electrical furnace with a length of 25 cm and an internal diameter of 3 cm. As this process was executed without any oxygen, high purity nitrogen (99.99%) with a volume flow rate of 200 ml min^{-1} was flowed through the furnace before the 30-min process began (Fig. 1). The furnace temperature was increased at a rate of 7 °C min^{-1} until it reached 400 °C, and this temperature was maintained for 90 min. The furnace was then switched off, and the product was intact until it reached room temperature. Nitrogen was flowing through the furnace for the entire duration of the process. The activated carbon produced was then washed with hot distilled water to remove the remaining phosphoric acid and was placed in an air oven (at 80 °C for 24 h) for complete drying. The yield of activated carbon production can be calculated by following equation:

$$CY(\%) = \frac{W_{AC}}{W_{RM}} \times 100 \quad (1)$$

where CY is carbon yield, W_{AC} and W_{RM} are activated carbon weight and raw material weight respectively.

Textural characterization of activated carbon was carried out by N_2 adsorption–desorption isotherms at 77 K using a surface area analyzer with Quadra Chrome adsorption instrument. Surface area, S_{BET}, was calculated by N_2 isotherms using the Brunauer–Emmett–Teller (BET) equation. Total pore volume, V_T, was the volume of liquid nitrogen adsorbed at the relative pressure of $P/P_0 = 0.95$. Average pore diameter, D_p, was calculated by Barrett–Joyner–Halenda (BJH) equation. To show the structural characteristics and investigate the morphology of the adsorbent, field emission scanning electron microscopy (FE-SEM) was used. In addition, the Fourier transform infrared spectroscopy (FT-IR) analysis was conducted to evaluate the functional groups in the adsorbent surface before and after adsorption. FT-IR spectra were obtained under vacuum condition at 400 °C in the range of 400–4000 cm^{-1}.

2.3. Effect of adsorbent dosage

In order to determine optimum adsorbent dosage, 50 ml of TC at a concentration of 100 mg L^{-1} was poured into 12 flasks. A different amount of activated carbon, ranging from 0.005 to 0.3 g, was then added to each flask. The flasks were then placed on a shaker with an angle velocity of 150 rpm for 24 h to ensure that the adsorption process reached equilibrium. The removal percentage (R%) of TC from solution was calculated by the following equation.

$$R\% = \left[\frac{(C_0 - C_e)}{C_0}\right] \times 100 \quad (2)$$

where C_0 and C_f are the initial and final concentrations of TC (mg L^{-1}), respectively.

2.4. Determination of point of zero charge (pH_{pzc})

The pH_{pzc} represents an electrical balance between adsorbent surface and solution. This value is useful for analyzing the effect of solution pH on adsorption capacity. Zero charge point of AC_{AS} was determined based on solid addition method (Mall et al., 2006). A total of 60 ml of 0.1 M KNO_3 salt was poured into 11 different flasks. The acidity (pH) of each flask was adjusted exactly from 1 to 11, by adding either 1.0 N HCl (strong acid) or 1.0 N NaOH (strong base) using a calibrated pH meter. The addition of an acid or base agent should not change the volume of the solution. The optimum dosage of adsorbent, determined in Section 2.3, was added to all 11 flasks, and they were placed on a shaker for 24 h to ensure that the charges