Research article

Removal of acetaminophen from synthetic wastewater in a fixed-bed column adsorption using low-cost coconut shell waste pretreated with NaOH, HNO₃, ozone, and/or chitosan

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ABSTRACT

Acetaminophen (Ace) is a trace pollutant widely found in sewage treatment plant (STP) wastewater. We test the feasibility of coconut shell waste, a low cost adsorbent from coconut industry, for removing Ace from synthetic solution in a fixed-bed column adsorption. To enhance its performance, the surface of granular activated carbon (GAC) was pre-treated with NaOH, HNO₃, ozone, and/or chitosan respectively. The results show that the chemical modification of the GAC's surface with various chemicals has enhanced its Ace removal during the column operations. Among the modified adsorbents, the ozone-treated GAC stands out for the highest Ace adsorption capacity (38.2 mg/g) under the following conditions: 40 mg/L of Ace concentration, 2 mL/min of flow rate, 45 cm of bed depth. Both the Thomas and the Yoon-Nelson models are applicable to simulate the experimental results of the column operations with their adsorption capacities: ozone-treated GAC (20.88 mg/g) > chitosan-coated GAC (16.67 mg/g) > HNO₃-treated GAC (11.09 mg/g) > NaOH-treated GAC (7.57 mg/g) > as-received GAC (2.84 mg/g). This suggests that the ozone-treated GAC is promising and suitable for Ace removal in a fixed-bed reactor.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), internationally recognized as one of emerging contaminants, possess serious threats to our well-being due to their toxicological properties (Fu et al., 2017; Yanyan et al., 2017). Among the PPCPs, acetaminophen (Ace), commonly used for treating fever (Vilve et al., 2010; Zhu et al., 2016), exists at trace concentrations, ranging from 100 μg/L to 1 mg/L (Zhuo et al., 2017; Fang et al., 2017). If not properly treated, aquatic organisms in water body are exposed to Ace contamination. Therefore, it is necessary to treat wastewater laden with Ace prior to its discharge (Ghanem et al., 2016; Ni et al., 2016; Albadarin et al., 2017a).

In recent years, advanced oxidation processes (AOP) have been extensively applied for PPCP removal from contaminated water (Kurniawan et al., 2006a, 2018). During the treatment, ·OH could indiscriminately degrade target compounds into smaller and more biodegradable oxidation by-products, CO₂ and H₂O. However, by-products like quinine and catechol may be more toxic than their original contaminants. In addition, AOP is not cost-effective when the concentration of target pollutant is low, while the volume of wastewater is large.

Like AOP, adsorption can remove organic compounds from aqueous solutions. Due to its excellent adsorption properties and affinity toward hydrophilic pollutants, granular activated carbon (GAC) is one of the most promising options for this purpose (Kurniawan and Lo, 2009; Kurniawan et al., 2010a, 2011; Babel and Kurniawan, 2003). The adsorbent, used in this study, originated from coconut shell waste, an agricultural by-product from coconut industry. Its conversion into activated carbon that can be used as a low cost material for water

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purification not only adds to its economic value, but also minimizes the cost of solid waste disposal into local landfills. The exchange properties of the coconut shell waste are due to the oxygen-containing surface functional groups like carboxylic and carbonyl (Babel and Kurniawan, 2004), which affect its adsorptive properties.

To improve its performance, the GAC needs to be chemically modified. Oxidation is effective to attach oxygenated complexes such as carboxyl, lactone and phenol on the carbon surface (Albadarin et al., 2017b; Repo et al., 2009, 2010; Kurniawan and Sillanpää, 2012; Kurniawan et al., 2006b) and to enlarge its surface area for adsorbing more pollutants, while pretreatment using NaOH may increase the concentration of oxygenated basic complexes on its surface. Due the presence of free amine ($-NH_2$) group in its C2 position, chitosan, another low-cost adsorbent from fishery waste, was used to coat the GAC for improving its affinity toward the target pollutant.

A preliminary study in batch modes has been conducted to assess the feasibility of carbon materials for this purpose (Yanyan et al., 2018). However, the study could not give accurate scale-up data because adsorption in a fixed-bed column is not at equilibrium, considering that the GAC rarely becomes exhausted in commercial process prior to its regeneration. Although adsorption isotherm, obtained from equilibrium data of batch studies, is suitable for obtaining operational parameters before column studies, this cannot reveal chemical changes that may take place during the treatment (Lemus et al., 2017).

In a practical study, a fixed-bed column needs to be adopted in order to design desired technical systems, as this could provide reliable data on breakthrough time, loss of adsorption capacity during subsequent cycles, and an acceptable flow rate. Unlike batch studies, a column operation, undertaken by Abdullah et al. (2016) using real brewery wastewater, could accurately quantify the adsorption capacity of an adsorbent for target pollutants. Hence, there is a growing need to perform a fixed-bed column for Ace adsorption from solutions using the treated GACs.

This article investigates the removal of Ace from synthetic wastewater in a fixed-bed column adsorption using GAC, an agricultural waste from coconut industry. To improve its removal, the adsorbent was pretreated with NaOH, HNO_3, ozone, and/or chitosan respectively. The effects of flow rate, influent Ace concentration and bed depth on Ace removal are studied, while its characteristics before and after their surface modification are analyzed using FTIR and SEM. The adsorption mechanisms of Ace by the treated adsorbents are also presented. Both the Thomas and the Yoon-Nelson kinetic models are employed to simulate experimental data for evaluating their column performance on Ace.
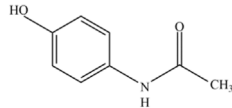
2. Materials and methods

2.1. Materials

The GAC has a surface area ranging from 900 to 1000 m^2/g (Table 1). Other chemicals, obtained from Sigma Aldrich (China), were of analytical grade. Ace, provided by Acros (New Jersey, USA), was used as a source of pollutant in synthetic wastewater (Table 2). The stock solution of Ace was freshly prepared by dissolving 1 g of the chemical in 1 L of deionized water. Working solutions were prepared by

Table 1
Properties of GAC.

Properties	GAC
Particle size (mm)	0.50
Pore volume (mL/g)	0.73
Total surface area (m^2/g)	900–1000
Solid density (g/cm^3)	0.48
Packing density (g/cm^3)	0.53
pH $_{PZC}$	8.9

Table 2
Properties of Ace.
Source: (Tao et al., 2015)

	λ_{max} (nm)	Molecular weight (g/mol)	Solubility (g/L, 20 °C)	pKa	Molecular Structure
Ace	243	151.16	14	9.5	

diluting the same stock solution to a predetermined concentration in the range of 40–120 mg/L. The initial pH of the Ace solution was measured using a pH-meter (model Mettler FE 20, Switzerland).

2.2. Pretreatment and characterization of GAC

2.2.1. Alkali pretreatment of GAC with NaOH

To increase oxygen-containing functional groups on its surface, GAC was pretreated with NaOH. About 20 g of GAC and 100 mL of 0.1 M NaOH was mixed. The suspension was shaken at 200 rpm for 3 h. The samples were separated from the solution and thoroughly washed with deionized water until the pH of the solution became neutral. Finally, the adsorbent was dried in an oven at 105 °C and stored in a desiccator prior to its use (Kurniawan et al., 2011).

2.2.2. Oxidation of GAC with HNO₃

Oxidation of GAC was undertaken at ambient temperature by adding 20 mL of 65% HNO_3 into 20 g of the adsorbent. After the reactor was shaken at 100 rpm for 3 h, the mixture was cooled and washed with deionized water. The adsorbent was then dried and stored in a desiccator (Kurniawan et al., 2010a).

2.2.3. Coating GAC with chitosan

To form a coating on GAC surface, 10 g of chitosan flakes (95% deacetylation) were diluted in 1% (v/v) acetic acid. The mixtures were agitated for 24 h to acquire a homogenized gel. Subsequently, the GAC was dipped into the gel, where the dose ratio of chitosan and GAC = 1:3 and then gently shaken overnight. The gel-coated adsorbent was washed with deionized water and dried. The process was repeated until the formation of a thick coating of chitosan on the carbon surface. The coated activated beads were removed and neutralized by putting them in 0.1% NaOH (w/v) solution for 3 h (Babel and Kurniawan, 2004).

2.2.4. Ozonation of GAC

In this pretreatment, the GAC was oxidized with ozone, produced by an ozone generator (model WH-X-10, Nanjing, China). While the samples were placed in a glass column with an internal diameter (id) of 1.5 cm and height (h) of 60 cm, the gaseous ozone passed through them at an inflow concentration of 5 mg/L and a flow rate of 1.6 L/min (total ozone mass: 8 mg/min). After 3 h, the GAC were washed with deionized water, dried in an oven at 105 °C for 24 h and stored in a desiccator (Kurniawan et al., 2006a).

2.3. Characterization of GAC before and after pretreatment

To identify changes that occurred in the surface of GAC after its pretreatment, Fourier transformation infrared (FTIR) studies were undertaken using a spectrometer model IS50 (Thermo, New York, US). To analyze the changes in its morphology before and after surface modification, the adsorbent's dry samples were analyzed using a scanning electron microscope (SEM) model ZEISS SIGMA (Germany), which operated at 15 kV. Its surface area was analyzed using a BET nitrogen