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MECHANISTIC INSIGHTS INTO ACETAMINOPHEN ADSORPTION ON CASHEW NUT SHELL BIOMASS-DERIVED ACTIVATED CARBONS

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Introduction

Thousands of drugs are approved for prescription use in the United States, and many of them end up in our water supply. Considering there are currently no federal or state regulations requiring drinking water or wastewater plants to monitor pharmaceutical compounds in water, many of these pharmaceuticals may pose a potential risk for both humans and aquatic life. Extensive research has been conducted on the removal of pharmaceuticals on activated carbons, where commercial activated carbons have been tested[1-3], as well as the carbons made of various biomass precursors[4-6]. This work focuses on the adsorption of acetaminophen on activated carbons made from cashew nut shell biomass, which was obtained from the cashew processing Sunshine Nut Company in Mozambique[7]. Acetaminophen is one of the most commonly used drugs in the US, where it is frequently detected in wastewater and surface water[8]. It is the principal cause of acute liver failure in humans[9], and a cause of multiple detrimental effects in aquatic life[10]. The objective of this study is to understand the effects of surface chemistry and porosity of cashew nut shell based activated carbons on the removal of acetaminophen, and to develop a detailed mechanism of adsorption.

Materials and Methods

Sample preparation: Shells were impregnated with H_3PO_4 solution at 1.7:1 ratio by weight, carbonized at 400-700°C in nitrogen gas, washed and dried. "CNP" stands for cashew, nut, and phosphoric acid. The number following the letters correspond to the carbonization temperature, i.e. at 400°C – CNP400. "E" stands for exhausted, after acetaminophen adsorption.

Acetaminophen adsorption: Ground activated carbons were combined with each concentration of acetaminophen solution (10-70 mg/L), and put on a shaker to equilibrate. The absorbance of filtrates was measured at 248 nm using Agilent 8453 UV–Visible Spectrophotometer (Agilent Technologies). The experimental equilibrium data were fit to Langmuir and Freundlich models.

Nitrogen sorption: Nitrogen adsorption/desorption experiments were performed at -196°C using an Automatic Volumetric Sorption Analyzer (Autosorb-1MP, Quantachrome Instruments).

Potentiometric titration: Measurements were performed with an automatic titrator (Mettler Toledo T50), using volumetric standard 0.1 M NaOH. The experimental titration curves were transformed into proton binding curves and pK_a distributions obtained using the SAIEUS procedure[11].

Fourier transform infrared (FT-IR) spectroscopy: Spectra were obtained in a Nicolet iS10 FT-IR Spectrometer (Thermo Fisher Scientific®), using ATR attachment.

X-Ray photoelectron spectroscopy (XPS): Measurements were performed on a Physical Electronic PHI 5700 spectrometer using non-monochromatic Mg-Ka radiation (300W, 15 kV and 1253.6 eV) The spectra obtained were analyzed using PHI ACESS ESCA-V6.0F software and processed using MultiPak 8.2B package.
Thermal Analysis: TG and DTG curves were obtained using a SDT (Q500) thermal analyzer.
Surface pH: Carbon powder was mixed with de-ionized water, and equilibrated. The pH of the suspension was measured using Piccolo ATC pH tester (Hanna Instruments).

Results and Discussion

The results of potentiometric titration (Table 1) and XPS showed that activated carbon obtained at 600°C has a higher amount of strongly acidic surface functional groups (pK_a~3-5) than the carbon obtained at 400°C. Stronger acidic environment of CNP600 facilitates the hydrolysis of acetaminophen to p-aminophenol and its chemisorption on the surface (Figure 1). For CNP400, the predominant mechanism of acetaminophen adsorption on the surface is physiosorption via hydrogen bonding.

Table 1. Number of surface functional groups for activated carbons obtained at 400 and 600°C

T °C	pK_a 3-5 mmol/g	pK_a 6-7 mmol/g	pK_a 8-11 mmol/g
400	0.561	0.955	0.371
600	0.726	0.290	0.169

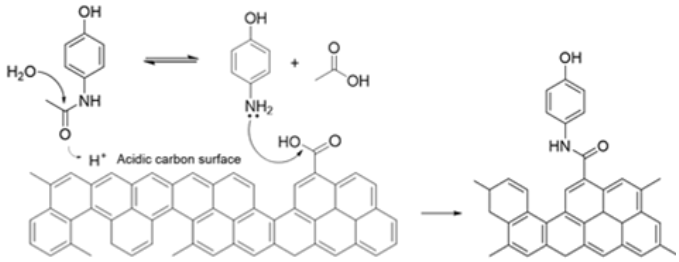

Figure 1. Acid hydrolysis of acetaminophen.

The high density of acidic surface functional groups on CNP400 (Table 2) results in group dimerization, surface coverage and steric phenomena. Adsorbed acetaminophen molecules will also dimerize via hydrogen bond formation and π stacking (Figure 2). Furthermore, the increase in the volume of micropores for CNP400 upon acetaminophen adsorption indicates the conversion of some narrow mesopores into micropores due to the surface changes and the retained dimers on the surface. As a result, the adsorption capacity of CNP400 is lower than that for CNP600. For the latter one, higher surface area and pore volume in combination with less densely populated surface result in more acetaminophen molecules being adsorbed, mainly inside the micropores.

Table 2. Maximum adsorption capacity, density of acidic surface functional groups, and volume of micropores for activated carbons obtained at 400 and 600°C

T °C	Q_{max} mg/g	d_{ASFG} mmol/m^2	V_{mic}/ $V_{mic}E$ cm^3/g
400	90	5.0	0.140/0.198
600	146	2.1	0.182/0.121

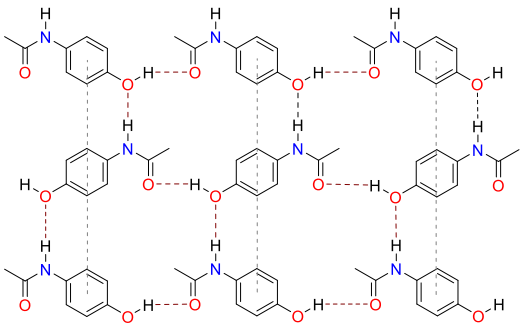

Figure 2. Dimerization of adsorbed acetaminophen molecules.

Conclusions

Removal of acetaminophen on cashew nut shell biomass-derived activated carbons is primarily driven by their surface characteristics, provided they possess high surface area accessible via micro/mesopores of appropriate size. Extent of surface acidity governs the mechanism of acetaminophen removal. High amount of strongly acidic groups, i.e. carboxylic, facilitates the hydrolysis of acetaminophen. Lower amount of strongly acidic groups causes the majority of acetaminophen being removed via physisorption. The high density of acidic surface functional groups results in their dimerization, pore blockage and steric phenomena. Carbon with the highest surface area/pore volume and density of acidic functional groups ~ 2 mmol/m^2 has the highest adsorption capacity for acetaminophen.

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