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# Investigation of adsorption of *p*-cresol on coconut shell-derived activated carbon

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## ABSTRACT

Mitigation of odorous volatile organic compounds, such as *p*-cresol from wastewater needs simple and practical technologies such as adsorption. In this research, an NaOH-activated carbon was prepared from coconut shell (CSAC-SH). Characterization of CSAC-SH suggested that the adsorbent possessed a well-developed microporous/mesoporous structure. To evaluate the performance of CSAC-SH, a series of batch experiments were conducted to investigate the effects of contact time (0–24 h), initial concentration (50–1000 mg L<sup>-1</sup>) and adsorbent dosage (1–20 mg L<sup>-1</sup>) on adsorption of *p*-cresol. The equilibrium data were found to conform to Redlich–Peterson, Fritz–Schluender, and Langmuir isotherms. The maximum monolayer adsorption capacity of 256.9 mg g<sup>-1</sup> (298 K) suggested that the prepared adsorbent has a high affinity toward *p*-cresol. A second-order kinetic model best described the experimental data and adsorption was governed by intraparticle diffusion. The thermodynamic analysis suggested that the adsorption was feasible, spontaneous, and exothermic (298–328 K). Furthermore, a desorption study suggested that chemisorption was dominant in the adsorption process. Results indicate that sodium hydroxide-activated carbon is effective in mitigating *p*-cresol from wastewater.

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## 1. Introduction

*p*-cresol (4-methylphenol) is one of the most malodorous emissions from intensive swine operations. It is also an increasing environmental nuisance, particularly in rural areas [1]. In addition, it is prevalent in wastewaters generated from paint, pesticide, petroleum, coal conversion, polymeric resin and phenol-producing industries [2,3]. As a highly toxic derivative of phenol, *p*-cresol is detrimental even at low concentrations and it has been classified by Environmental Protection Agency (EPA) as a possible carcinogen [4]. Hence, mitigation of *p*-cresol from water bodies is receiving more attention.

Adsorption of contaminants by activated carbon has been identified as one of the most effective and feasible technologies owing to activated carbons' microporous nature, favorable pore size distribution, high surface reactivity, large adsorption capacity, versatility and easy availability [3,5]. Activated carbon may be prepared using a variety of raw materials. However, there has been an increasing interest in using lignocellulosic by-products including agricultural residues and coconut shells as raw materials [6–8].

Recently, Martins et al. [10] reported that activated carbon prepared using NaOH provided a high surface area equipped with

basic functional groups which resulted in high adsorption capacities for tetracycline reduction. In another study conducted by the same group of Cazetta et al. [11], it was reported that NaOH-activated carbon performed well for uptake of methylene blue. Moreover, Tan et al. [12] modified commercial activated carbon with NaOH and it was found to be a state-of-the-art adsorbent for CO<sub>2</sub> removal and they explained that NaOH helped to change the morphological structural and reduce the acidity of the carbon surface by replacing carboxylic and phenols ions with Na<sup>+</sup>. Based on these studies, we hypothesized that NaOH-activation process is also capable of yielding a highly active adsorbent for mitigation of *p*-cresol.

The objectives of the present work were to characterize the physiochemical-NaOH-activated carbon prepared from coconut shell, investigate the adsorption properties of the adsorbent for removal of *p*-cresol, and study the kinetics, equilibrium, mechanism, and thermodynamics of the adsorption. A desorption study was also carried out to obtain further insights into the nature of adsorption of *p*-cresol onto the adsorbent.

## 2. Materials and methods

### 2.1. Preparation of coconut shell based activated carbon

The coconut shell used in this research was obtained locally. The preparation method and instruments employed in the present

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research were similar to those reported earlier for preparation of ZnCl<sub>2</sub> treated coconut shell-activated carbon (CSAC-ZnCl<sub>2</sub>) by the authors [6]. Initially, the coconut shell was crushed into small pieces with a particle size of about 10 mm and was placed in a horizontal stainless steel reactor and carbonized at 673 K for 1 h with a nitrogen flow rate of 2 L min<sup>-1</sup> in a horizontal kiln (Sentry Xpress 4.0, Paragon) at a heating rate of 10 C min<sup>-1</sup>. This semi-finished product was named Char-400. Subsequently, the Char-400 was ground and sieved through a 5 mm screen before mixing with sodium hydroxide pellets (≥ 97.0 %, Acros) with NaOH: char impregnation ratio (IR) of 1:1 for 3 h and dried overnight at 383 K after removing the supernatant liquid. Further, the char sample was pyrolyzed (1273 K for 1.5 h) and allowed to cool down to room temperature under nitrogen atmosphere followed by washing with hot deionized water and overnight dehydration (343 K) to obtain the final product, named CSAC-SH.

## 2.2. Characterization of activated carbon

The structure and morphology of the adsorbents were characterized via scanning electron microscopy (SEM). The SEM images were recorded using a Hitachi Model S-3200 N apparatus.

The Brunauer–Emmett–Teller surface area (*S*<sub>BET</sub>) of the adsorbents was determined from the nitrogen adsorption isotherms at 77 K using an automatic BET analyzer (Micrometrics Gemini VII 2390p).

The surface of the activated carbon samples was studied via Fourier transform infrared spectra (FTIR) recorded at 4 cm<sup>-1</sup> of resolution and 64 scans min<sup>-1</sup> between 4000 and 500 cm<sup>-1</sup> using a Perkin-Elmer RXI FTIR spectrometer. The raw material of coconut shell was analyzed in a Bruker Platinum ATR spectrometer.

The acid value of the activated carbon was measured from the pH of a solution containing 0.4 g activated carbon and 20 mL deionized water after shaking at 400 rpm for 12 h [13].

The surface functional groups of the activated carbon were determined using the Boehm titration [14]. The procedure was the same as described in a previous paper [6].

## 2.3. Batch adsorption of *p*-cresol on CSAC-SH

Experimental *p*-cresol solutions of desired concentrations (50–1000 mg L<sup>-1</sup>) were prepared from the stock solution with appropriate dilutions. Typically, 0.5 g of CSAC-SH was weighed and added into 100 mL aliquots of *p*-cresol solutions in 150 mL serum bottles, which were covered with rubber stoppers and sealed with 20 mm aluminum air-tight caps, and were placed on an isothermal hot plate and agitated at 100 rpm. The *p*-cresol concentrations in the supernatant solutions before and after adsorption were determined using a UV spectrophotometer (Genesys 10S, Thermo Scientific) at its maximum wavelength ( $\lambda$ ) of 277 nm. All batch adsorption experiments were performed in duplicates. A blank of the same *p*-cresol concentration without adsorbent following the identical procedure was monitored in every experiment to confirm that the adsorbate is neither volatilized nor adsorbed on the walls of serum bottles. The equilibrium amount of *p*-cresol adsorbed,  $q_e$  (mg g<sup>-1</sup>), and the percent removal, *X* (%) were calculated by Eq. (1) and Eq. (2), respectively [3]:

$$q_e = \frac{(C_o - C_t)V}{W} \quad (1)$$

$$X (\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

where *C*<sub>o</sub>, *C*<sub>t</sub>, and *C*<sub>e</sub> (mg L<sup>-1</sup>) are the initial, any given time, and equilibrium liquid phase concentrations of *p*-cresol, respectively. *V* (L) is the volume of the solution, and *W* (g) is the mass of the dry CSAC-SH used.

**Table 1**  
Kinetic and isotherm models for adsorption.

Kinetic model names	Expression
Pseudo-first-order	$q_t = q_e [1 - e^{-k_1 t}]$ (3)
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ (4)
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$ (5)
Intraparticle diffusion	$q_t = K_{id} t^{0.5} + C$ (6)
Isotherm model names	Expression
Freundlich	$q_e = K_f C_e^{1/n}$ (7)
Langmuir	$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$ (8)
Redlich–Peterson	$q_e = \frac{A C_e}{1 + B C_e^\beta}$ (9)
Temkin	$q_e = \left( \frac{RT}{b_T} \right) \ln(\alpha C_e)$ (10)
Fritz–Schluender	$q_e = \left( \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}} \right)$ (11)
Radke–Prausnitz	$\frac{1}{q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/n_1}}$ (12)

where  $q_t$  (mg g<sup>-1</sup>) and  $q_e$  (mg g<sup>-1</sup>) = the amount of adsorbate adsorbed at any time and at equilibrium on adsorbent, respectively;  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) = pseudo-first-order and pseudo-second-order adsorption rate constants;  $h$  (mg g<sup>-1</sup> min<sup>-1</sup>) =  $k_2 q_e^2$  = initial adsorption rate;  $\alpha$  (mg g<sup>-1</sup> min<sup>-1</sup>) and  $\beta$  (g mg<sup>-1</sup>) = Elovich constants;  $k_{id}$  (mg g<sup>-1</sup> min<sup>-0.5</sup>) = intraparticle diffusion constant; *C* (mg g<sup>-1</sup>) = the thickness of the boundary layer.  $K_f$  (mg g<sup>-1</sup> (L mg<sup>-1</sup>)<sup>1/n</sup>) = Freundlich constant; *n* = constant in Freundlich isotherm;  $Q_o$  (mg g<sup>-1</sup>) = maximum monolayer adsorption capacity;  $K_L$  (L mg<sup>-1</sup>) = Langmuir constant; *A* (L g<sup>-1</sup>), *B* (L mg<sup>-1</sup>) and  $\beta$  = Redlich–Peterson constants; *R* (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) = universal gas constant; *T* (K) = absolute solution temperature;  $\alpha$  (L g<sup>-1</sup>) = equilibrium binding constant;  $\theta$  (J mol<sup>-1</sup>) =  $RT/b_T$  = Temkin constant related to the heat of adsorption;  $\alpha_1$  ((mg g<sup>-1</sup>)/(mg L<sup>-1</sup>) <sup>$\beta_1$</sup> ),  $\alpha_2$  ((mg L<sup>-1</sup>) <sup>$\beta_2$</sup> ),  $\beta_1$  and  $\beta_2$  = Fritz–Schluender constants;  $K$  (L g<sup>-1</sup>),  $k$  (mg g<sup>-1</sup>) (L (mg<sup>-1</sup>)<sup>1/n</sup>) and  $n_1$  = Radke–Prausnitz constants.

## 2.4. Kinetic modeling and equilibrium modeling of *p*-cresol removal

Experimental data were fitted to different kinetic and isotherm models, as given in Table 1 of Eq. (3) to Eq. (6) [11,15] and of Eq. (7) to Eq. (12) [3,4], respectively.

## 2.5. Thermodynamic modeling

Adsorption thermodynamics were studied with initial *p*-cresol of 500 mg L<sup>-1</sup> at different temperatures of 298 K, 308 K, 318 K and 328 K with 5 g L<sup>-1</sup> CSAC-SH and agitated at 100 rpm. The thermodynamic parameters including Gibbs free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ), were determined from the following equation [3]:

$$\Delta G^\circ = -RT \ln K_e \quad (13)$$

where *R* (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant. *T* (K) is the temperature, and  $K_e$  is the distribution coefficient. The  $K_e$  value

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