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Adsorbents from pine wood via K_2CO_3-assisted low temperature carbonization for adsorption of *p*-cresol

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ABSTRACT

A low-temperature carbonization process was evaluated to synthesize an inexpensive adsorbent from pine wood to mitigate *p*-cresol from aqueous system. Surface response experiments using carbonization time, impregnation ratio (IR), and carbonization temperature as variables indicated that optimum adsorbent yield and adsorption were 63.22% and 5.40 mg g^{-1}, respectively at carbonization temperature of 266 °C, IR of 2, and carbonization time of 2 h. The equilibrium adsorption data agreed with Langmuir's model and maximum theoretical adsorption of 6.97 mg g^{-1} was obtained at temperature 25 °C, unadjusted pH and adsorbent dose of 10 g L^{-1}. The kinetic analysis combined with desorption study revealed that *p*-cresol chemisorbed on the adsorbent surface. Additionally, adsorption of *p*-cresol was found to be exothermic and inhibited by presence of surface acidic oxygen groups.

1. Introduction

Animal agriculture, especially swine farming is a major source of emission of volatile organic compounds (VOCs) (Blanes-Vidal et al., 2009). Among the VOCs produced, phenols (e.g., *p*-cresol), aldehydes (e.g., 2-methylbutrylaldehyde), and fatty acids (e.g., isovaleric acids) are considered to be malodorous (Schiffman et al., 2001). In addition, the VOCs tend to react with NO_x and from atmospheric ozone affecting plant, animal, and human health (Borhan et al., 2012). Hence there is a significant interest in mitigating these compounds from animal housing operations (Blunden and Aneja, 2008).

Among various physical and chemical processes available for removal of organic compounds, adsorption is considered as one of the favorable methods available owing to its simplicity in operation, efficiency, and economics (Radovic et al., 2000; USEPA). Usually activated carbon is used as an adsorbent due to favorable surface chemistry. However, due to high cost of raw materials for synthesis of activated carbon, researchers have turned their focus on utilizing low-cost precursors for production of activated carbon. For example, micro-algal biomass (Aravindhan et al., 2009), coconut husk (Foo and Hameed, 2012b), wood particleboard wastes (Girods et al., 2009), corn (Park et al., 2010), dates stones (Alhamed, 2009), avocado kernel seeds (Rodrigues et al., 2011), tobacco residues (Kilic et al., 2011), activated sludge (Li et al., 2012) have been used as precursors to synthesize activated carbon for removal of phenols.

Another inexpensive resource is pine, which is abundantly grown in the southeastern United States. Several researchers have studied synthesis of pine-based adsorbents using salts of zinc, potassium, etc. for removal of variety of pollutants from water (Tseng et al., 2003; Mohan et al., 2007, 2011; Calvete et al., 2009, 2010; Ofomaja and Naidoo, 2011; Zhou et al., 2010). However, most of the aforementioned studies focused on removal of heavy metals and a few on phenolics.

In addition, most studies involved use of high temperatures (>500 °C) for manufacture of the adsorbent thus making the entire processes uneconomical for commercial-scale production. If adsorption were to be the accepted by agricultural industry as a preferred technology, the entire process has to be inexpensive and practical such that adsorbents could be prepared on site. Further, it is also important to determine the performance of such inexpensive adsorbents when exposed to pollutant mixtures that are commonly found in swine facilities. Hence, the goal of this research is to evaluate low-temperature activation process (266–435 °C) for synthesis of adsorbents from pine wood that could be used for abatement of organic pollutants produced in swine farming. For this research we chose *p*-cresol as a representative VOC due to its consistent occurrence in swine barns and its adverse effects on human health (Schiffman et al., 2001; Wu et al., 1999; Singh et al., 2008). We focused on synthesis of pinewood activated char (PAC) by specifically studying (1) the effects of carbonization time, impregnation

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Table 1
Experimental factors and coded levels of independent variables employed in synthesis of PAC.

Factors	Code	Coded variable levels				
		$-\alpha$	−1	0	1	$+\alpha$
Temperature (°C)	X_1	265.91	300	350	400	434.08
Hold time (h)	X_2	1.59	1.5	2	2.5	2.84
IR	X_3	0.32	1	2	3	3.68

ratio (IR), and carbonization temperature on adsorbent yield and capacity (2) characterize the surface of the adsorbent, (3) study adsorption kinetics and isotherms, (4) determine the effect of 2-methylbutrylaldehyde on adsorption of *p*-cresol, and (5) confirm the role of dissolved and surface oxygen on adsorption of *p*-cresol.

2. Experimental methods

2.1. Preparation of activated char

Wood chips of Loblolly pine (*Pinus taeda*), grown in North Carolina, USA, were used as a precursor. Based on our preliminary studies, K_2CO_3 (purity 99%, Fisher scientific) was chosen as activating agent. The pine wood was soaked in K_2CO_3 solution for 8 h as described by Ahmad and Alrozi (2010). Various impregnation ratios (IR) (K_2CO_3/wood) were tested to determine the effect of K_2CO_3 loading on yield and adsorption capacity of pinewood activated char (PAC). After impregnation for 8 h, pine wood was washed thoroughly for 45 min. Subsequently these samples were dried at 70 °C for 12 h. Activation of these dried K_2CO_3 impregnated samples was carried out at temperature (300–400 °C) with a carbonization time of (1.5–2.5 h) under nitrogen flow (2 L) at heating rate of 10 °C min^{-1}.

2.2. Experimental design

A central composite design (CCD) consisting of 2^3 factorial levels and 2×3 axial levels and 6 center points was used to assess the effects of carbonization temperature, carbonization time, and IR on PAC yield and adsorption capacity. For our studies carbonization temperature, carbonization time and IR were set at 300–400 °C, 1.5–2.5 h and 1–3, respectively. Additional details of the experimental design are presented in Table 1.

2.3. Characterization of PAC

Specific surface areas of PAC and the original pine wood were determined by Brunauer–Emett–Teller (BET) analyzer (Micrometrics Gemini VII 2390). Samples were degassed at 150 °C for 2 h prior to the analysis and the nitrogen desorption was performed at 77 K. The morphological features and elemental composition were examined via variable pressure scanning electron microscope (5 keV) (Hitachi S-3220) equipped with a secondary electron detector. The raw data was processed using revolution software (4pi analysis Inc., Durham, NC).

The acid value was determined by measuring the pH of equilibrated solution (8 h) of 0.4 g of activated char and 20 mL of de-ionized water (Sayed and Bandosz, 2004). The point of zero charge (PZC) of the pine wood and PAC was determined as described by Lopez-Ramon et al. (1999) and Nethaji et al. (2010). Finally, the surface functional groups were characterized via Boehm titration procedure (Boehm, 1966). Briefly, 1 g of PAC (or pine wood) was contacted with 50 mL of HCl, NaOH, Na_2CO_3 and $NaHCO_3$ (0.05 M each) for 24 h followed by titration with NaOH and HCl (0.05 M each) using phenolphthalein and methyl orange as indicators.

2.4. Adsorption studies

100 mL of *p*-cresol solution (100 mg L^{-1}) was mixed with 1 g of PAC in serum bottles on a temperature-controlled hot plate. The contents of the serum bottles were agitated at 100 rpm via a magnetic stirrer. Liquid samples were drawn periodically (0.5 mL every 15 min) and change in *p*-cresol concentration was quantified using a gas chromatograph equipped with a mass selective detector (Agilent Technologies, 7890 A) and a HP-5 MS column (30 m × 0.25 mm × 0.25 μm). Data was acquired using an oven temperature of 65–95 °C at 5 °C min^{-1} and a split ratio of 150:1 (1.2 mL min^{-1}) while injector and detector were maintained at 250 °C. All batch experiments were performed in 150 mL serum bottles in duplicates.

2.5. Adsorption kinetics and isotherms

The batch experimental data was analyzed via pseudo-first order (Eq. (1)), pseudo-second order (Eq. (2)), Elovich (Eq. (3)) and intra-particle diffusion models (Eq. (4)) as described by Wang and Li (2013), Demirbas et al. (2004), Allen et al. (2005), Singh and Pant (2004), and Das et al. (2012).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (2)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (3)$$

$$q_t = k_p t^{1/2} + C \quad (4)$$

In Eqs. (1) through (4), q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption of *p*-cresol at equilibrium and at any given time t (min) and k_1 (min^{-1}) and k_2 (mg g^{-1} min^{-1}) are the first and second order rate constants which are obtained from the plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t. For Elovich model, α (mg g^{-1} min^{-1}) and β (g mg^{-1}) are the initial adsorption rate and desorption constants and for intra-particle diffusion, C is a constant.

In addition, to understand the effect of *p*-cresol concentration on adsorption capacity of PAC at a given temperature (Langmuir, 1916) (Eq. (5)) and (Freundlich, 1906) (Eq. (6)) isotherm models were tested whose linearized forms are as below.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (6)$$

where C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, q_e (mg g^{-1}) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. K_F and n are Freundlich's adsorption constants.

To determine the type of adsorption phenomenon involved i.e., physisorption or chemisorption, an additional desorption test was performed. Batch experiments (120 min) were conducted using DI water as desorbing agent and spent PAC from the previous experiments. Liquid samples were collected periodically and analyzed for *p*-cresol concentration.

2.6. Effect of 2-methylbutyraldehyde (2-MB)

In a typical swine lagoon, *p*-cresol co-exists with VOCs such as aldehydes, and volatile fatty acids. Hence, additional experiments were performed to study the competitive effect of *p*-cresol