

ABSTRACT

DAS, LALITENDU. Synthesis of Low Cost Adsorbent from Pine Wood for Mitigation of *p*-cresol. (Under the direction of Dr. Praveen Kolar.)

The goal of this research was to synthesize low-cost adsorbent for mitigation of *p*-cresol from swine farming operation. The objectives were to: (1) synthesize low-cost pine wood activated carbon (PAC) by optimizing carbonization time, impregnation ratio (IR), and carbonization temperature (2) characterize the PAC, (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. A central composite design was employed to study the effect of carbonization time, impregnation ratio (IR), and carbonization temperature on carbon yield and adsorption capacity. Optimum carbon yield and adsorption was found to be 63.22 % and 5.40 mg g⁻¹ respectively at a temperature of 266 °C, impregnation ratio of 2 and carbonization time of 2 hours. Characterization of the activated carbon was performed via scanning electron microscopy, Brunaur-Emmett-Teller surface area estimation. PAC's performance was tested in batch reactor and maximum theoretical adsorption capacity of 6.97 mg g⁻¹ was obtained at temperature 25 °C, unadjusted pH and adsorbent dose of 10 g L⁻¹. The kinetic studies indicated that adsorption of *p*-cresol molecules onto PAC followed Elovich and intra-particle diffusion model suggesting that adsorption of *p*-cresol proceeded via chemisorptions. Adsorption mechanism was supported by π - π interaction and adsorption decreased with increase in temperature suggesting exothermic nature of adsorption. In addition, surface oxygen inhibited adsorption of *p*-cresol perhaps due to enhancement of hydrophilicity.

Synthesis of Low Cost Adsorbents from Pine Wood for Mitigation of *p*-cresol

by
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BIOGRAPHY

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CHAPTER ONE

Introduction

Water pollution by organic compounds has increased tremendously due to increases in industrial and animal production activity. Odor emissions from livestock facilities affect surrounding community specifically rural areas. These communities are facing problems from emission of gases, odors, dust and microorganisms which is deteriorating the quality and health of rural people (Blanes-Vidal et al., 2009). With the rapid increase in concentrated animal feeding operations (CAFOs) emission of volatile organic compounds (VOCs) such as aldehydes, amines, volatile fatty acids (VFAs), indoles, phenols, cresols, sulfur-containing compounds, hydrocarbons, ketones, and others has gone up significantly (Schiffman et al., 2001). Environmental concerns associated with CAFOs are odor pollution from gaseous emissions into the ambient air, pollution of surface and ground waters with excess nutrients, and waste management due to decomposition of manure (Lovanh, 2009). From swine production systems, feces, urine, feed and wash water are stored in pits beneath the facility or in lagoons which are decomposed into odorous volatile organic compounds (Cook et al., 2010). The United States produces more than 22,000 million pounds of pork which accounts for 39% of world pork exports (USDA NASS 2008). North Carolina is the second largest producer in swine (USDA NASS 2010). Several studies have been done to identify odorants responsible for the odor emitted from swine slurry. Results reported on odor intensity have shown that the most important gases contributing to malodor are *p*-cresol, skatole, 4-ethylphenol and acetic acid (Blanes-Vidal et al. 2009). *p*-cresol is a malodorous compound

which is found not only in swine slurry but also in effluents from many chemical industries, like petrochemical, oil refinery and steel plants.

Technology for waste water treatment

Increases in population and industrialization have contributed tremendously to water pollution. Assessment and supply of good quality water has become a big challenge for water treatment plants. Suitable technology selection for water treatment is a complex task. The process technologies can be classified broadly into three categories physical, chemical and biological (Bhatnagar and Sillanpaa, 2010).

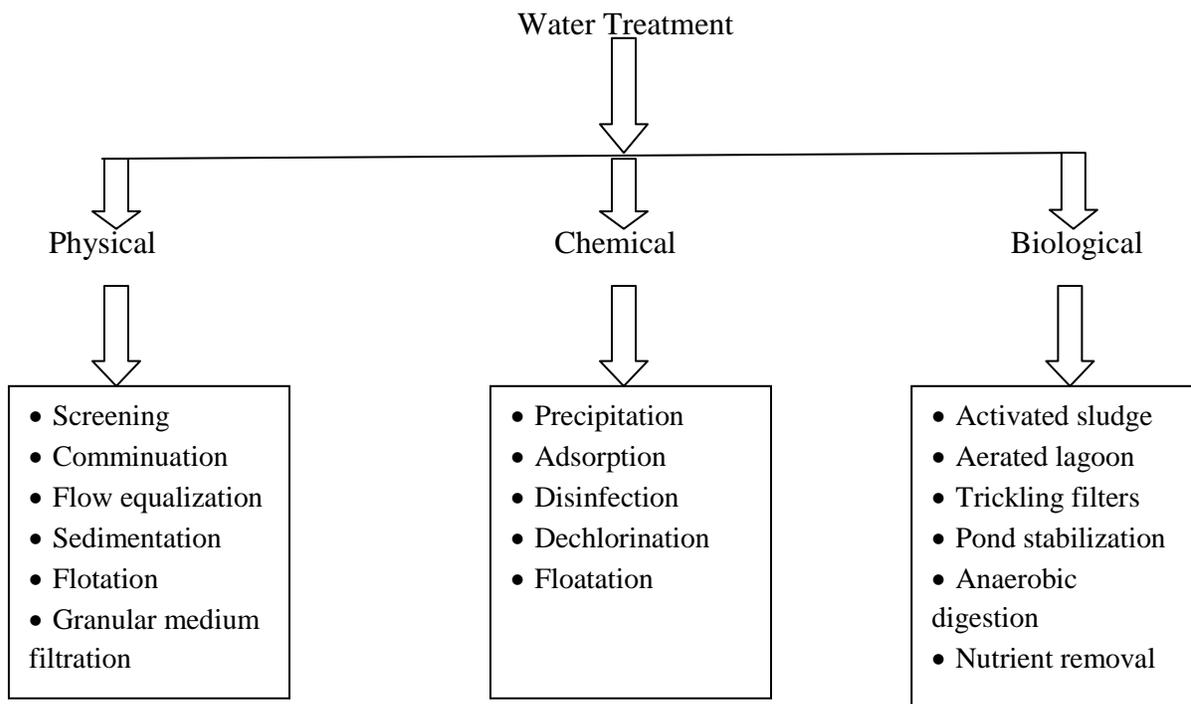


Figure 1.1: Waste water treatment classification

Most of the above mentioned processes require higher capital investment, so there is always an opportunity for low cost technique (Ahmaruzzaman, 2008). Adsorption is the favored technique over others because of its easy availability, widely studied mechanism, ease of operation, simplicity in design, wider application and non-formation of byproduct (Ahmaruzzaman, 2008; Bhatnagar and Sillanpaa, 2010).

Adsorption

Adsorption is the adherence of substance to the surface of another substance, which is suspended in two different phases. Two phases may be liquid-liquid, solid-liquid, liquid-gas, and solid-gas phase. Adsorption can be physical or chemical. Chemical adsorption is monolayer where as physical adsorption can be multi layer. Physical adsorption is driven purely on van der Waals interactions. Physical adsorption occurs at particular set of conditions and is a reversible process. High physical adsorption can be obtained at temperature close to the critical temperature of the gas where as chemical adsorption can be seen at temperatures much higher than the critical temperature (Dabrowski, 2001). A typical adsorption phenomenon is illustrated in Fig 1.2.

The kinetic mechanism of adsorption on heterogeneous solid surface is performed by four different steps 1) diffusion of adsorbate from the bulk phase to the surface of the adsorbent. 2) diffusion of molecules from surface to the inside of the pores 3). diffusion of molecules in the surface phase and 4). adsorption/desorption processes. (Dabrowski, 2001)

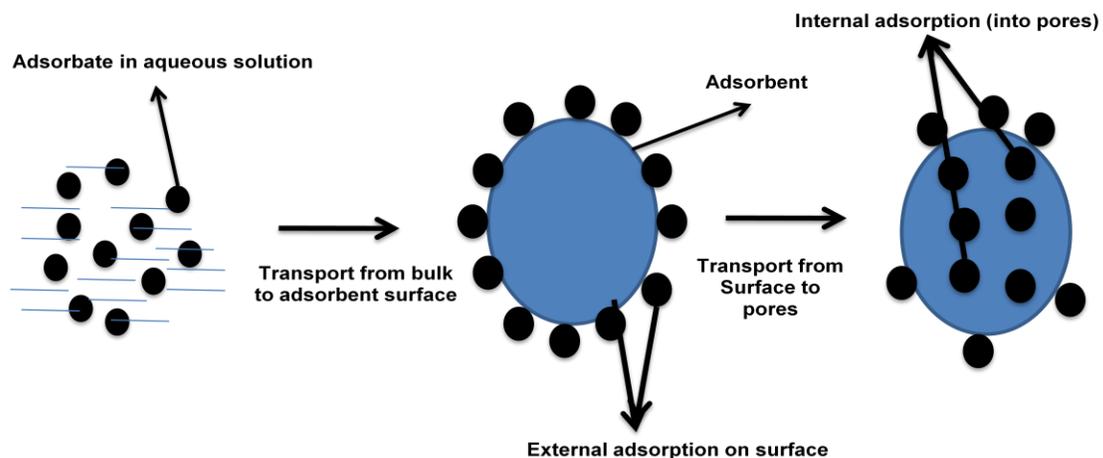


Figure 1.2. Illustration of adsorption phenomenon

Adsorption mechanism

Though much research has been done on adsorption, its phenomenon in liquid phase for aromatic compounds can be explained through three different mechanisms, 1) the π - π dispersion interaction mechanism 2) the hydrogen bonding formation mechanism 3) the electron donor-accepter complex mechanism.

Coughlin and Ezra (1968), proposed the π - π dispersion interaction mechanism. According to them electron is removed from the π -electron system due to acidic surface oxygen group. This weakens the interaction between π -electron of aromatic group and π -electron of the carbon, therefore uptake of the aromatic phenol group is reduced. In the same year Coughlin

and Ezra proposed that bonding of water molecules with selective functional oxide groups by hydrogen bonding plays a significant role in adsorption of phenolic compounds.

The electron donor-accepter complex mechanism was proposed by Mattson et al., (1969).

They said that carbonyl oxygen of the carbon acts as an electron donor where as aromatic rings of the adsorbate act as electron acceptor. Mattson and co workers explained that when carbon is oxidized, carbonyl groups are converted to carboxylic groups and the electron donor acceptor complex is broken, thus uptake of phenolic compounds is decreased.

Factors affecting adsorption

Adsorption in a liquid phase is dependent on many parameters (Hameed et al., 2008; Nasuha et al 2010; Boudrahem et al., 2009), which include:

- the nature of the adsorbent: pore structure, ash content, functional groups.
- the nature of the adsorbate: pKa, functional groups present, polarity, molecular weight, size.
- the solution conditions: pH, ionic strength, and the adsorbate concentration.

One of the important factors controlling the role of adsorption onto the adsorbent has been pH, which controls the distribution of charge on the adsorbent surface due to its interaction with the adsorbate ions. Uptake of adsorbents is influenced in a certain range of pH. Point zero charge (pH_{pzc}) determines the limiting pH of a solution. At this pH, surface of the adsorbent is neutral which attracts the adsorbate to the surface of adsorbent by diffusion (Noh

and Schwarz, 1989). The surface of the adsorbent becomes negatively charged at pH higher than pH_{pzc} attaching positively charged particles from the solution, but at pH lower than pH_{pzc} , negative ions from the solution are attached to the positively charged surface of the adsorbent (Haghseresht et al., 2003). Adsorption increases with increase in pH within certain limit (Kumar and Bandopadhyaya, 2006), further increase in pH decreases the adsorption where as some removal of adsorbates remain unaffected by pH for a particular range. (Lata et al., 2007; Nouri et al., 2002; Singh et al., 2007). Increase in adsorbent dose increases the adsorption capacity which can be explained due to an increase in number of active sites to adsorb more of adsorbate. Adsorption per unit mass decreases with increase in adsorption dose, this is due to presence of more unoccupied active sites due to constant concentration gradient of adsorbate (Kumar et al., 2007, Ahmaruzzaman and Sharma 2005). Increase in temperature, surface area and pore volume increases adsorption capacity (Auta and Hameed, 2011, Hamdeed et al., 2008, Tan et al., 2008).

Adsorption equilibrium model

Adsorption isotherm is a function of concentrations of the adsorbate in a solution at a given temperature. Isotherm tests are conducted using different models such as Langmuir, Freundlich, Dubinin-Radushkevich and Temkin & Pyzhev.

The Langmuir isotherm is valid for monolayer adsorption, the linear form of the equation is given by (Langmuir, 1916).

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

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, Q_0 (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants related to adsorption capacity and rate of adsorption respectively.

The Freundlich isotherm is an empirical model, the linear form of which is given by the equation (Freundlich, 1906)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad . \quad (2)$$

The value of $n > 1$ represents a favorable adsorption condition.

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, K_F (mg g⁻¹) (mg L⁻¹)^{-1/n} and n are adsorption capacity and Freundlich's adsorption constant respectively.

Dubinin-Radushkevich isotherm is based on the principle that it does not assume homogenous surface which can be given by the equation (Dubinin and Radushkevich, 1947)

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad . \quad (3)$$

where β is a constant and gives the mean free energy of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution.

The linear form of Temkin isotherm equation is as follows (Temkin and Phyzev, 1940)

$$q_e = B \ln K_T + B \ln C_e \quad . \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent.

Adsorption kinetic models

Efficiency of adsorption is studied from the mechanism of adsorption and kinetic parameters. Data is analyzed by pseudo-first order, pseudo-second order, Elovich model and intra-particle diffusion models. Selection of the order of reaction was based on the value of coefficient of determination (R^2).

Kinetic analysis of adsorption in the pseudo-first order rate equation is given by (Ajmal et al., 2003)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad . \quad (5)$$

where q_e is obtained from the equilibrium experiments. The plot of $\log(q_e - q_t)$ vs t should be linear.

The pseudo-second order kinetic model equation based on equilibrium is expressed as (Singh et al., 2006)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad . \quad (6)$$

The plot of (t/q_t) vs. t should be linear and from which k_2 and q_e can be obtained.

The Elovich equation is generally expressed as (Demirbas, 2004)

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad . \quad (7)$$

Data to follow Elovich model should yield a linear relationship when plotted between q_t and $\ln(t)$.

The intra-particle diffusion equation is expressed as (Kilic et al., 2011).

$$q_t = k_p t^{1/2} + C \quad . \quad (8)$$

Higher R^2 values determine the involvement of intra-particle diffusion process in adsorption.

Where q_e (mg/g) and q_t (mg/g) are the adsorption at equilibrium and at any given time t (min) and k_1 (1/min) and k_2 (mg/g 1/min) 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 the Elovich model, α (mg/g 1/min) and β (g mg⁻¹) are the initial adsorption rate and desorption constants and K_p is intra-particle diffusion constant and C is a constant

Adsorbents

Large numbers of commercial adsorbents are available in the market for treatment of waste water. Among them silica gel, activated alumina, zeolites and activated carbons are the few important ones. Activated carbon is the most popular among all these adsorbents for waste water treatment because i) it is porous nature ii) high adsorption capacity iii) better surface area and chemistry and iv) low cost and easy availability (Bhatnagar and Sillanpaa, 2010).

Activated carbons

Any material with high carbon content and low inorganics can be used in the production of activated carbon. This process involves two steps i) carbonization of the raw material below 800 °C in absence of oxygen ii) activating the carbonized product (activation of the carbonized material are done two ways mainly chemical and physical activation).

During this process most of the non carbon elements leave the material as volatile gases. Due to pyrolytic decomposition of the material, residual carbon atoms form into sheets of aromatic rings with planar structure which gives rise to pores that facilitate the adsorption phenomenon. (Bansal et al., 1988)

Salient features of materials to consider for activated carbon include (Bansal et al., 1988) 1) presence of high carbon content 2) low level of inorganic material 3) availability and cost of the materials 4) storage and durability of the materials.

Bansal et al., (1988) classified activated carbon as: powdered activated carbon, granulated activated carbon, spherical activated carbon, impregnated carbon, and polymer coated carbon.

Advantages of activated carbon

With regard to, A waste water treatment activated carbon is the preferred adsorbent. Salient features that are responsible for its popularity and efficiency are:

1. Highly micro-porous in nature, which will facilitate the mechanism of adsorption i.e., it will help in giving a passage to the adsorbate to enter into the pores (Killic et al., 2011).

2. Larger surface area in the range of 600-2000 m²/g giving rise to more active sites which can attach more adsorbate onto the activated sites (Bhatnagar and Sillanpaa, 2010).
3. It can remove a wide variety of pollutants such as phenols, metal ions, dyes, detergents, and pesticides (Ahmaruzzaman, 2008).
4. It is available easily and has high adsorption capacity (Kilic et al., 2011).

Despite all these advantages, use of activated carbon as the sole source for water treatment is restricted due to higher cost. As activated carbons are made from carbonaceous materials, in recent past great efforts have been made to look for low cost alternative adsorbents from waste products or materials that are abundant, cheap, easily available and that can be activated easily (Pollard et al., 1992). Many low cost adsorbents have been prepared from agricultural waste materials as well as industrial waste materials that are either adsorbate specific or adsorbent specific (Demribas, 2009).

Waste materials as adsorbents

Waste materials are suitable for preparation of activated carbon because 1) they are inexpensive and are environmentally friendly which are used for production of value added product 2) these are renewable in nature that is available in abundance 3) processing cost of these substances is inexpensive that makes it a suitable option for water treatment (Ahmedna

et al., 2000). Because of these advantages it is lucrative enough to utilize waste materials as a low cost activated carbon to solve environmental issues keeping the cost factor in control.

There are various sources of waste materials that can be used as low cost adsorbent, Such sources are broadly classified as i) agricultural waste ii) industrial waste iii) municipal waste iii) natural material.

Agricultural wastes that are rich in lignocelluloses are good sources of adsorbent for removal of various pollutants. Lignocelluloses are a rich source of cellulose hemicelluloses and lignin, apart from other functional groups like lipids, proteins, hydrocarbons, water and starch that are capable of removing organic pollutants and heavy metals (Ioannidou and Zabaniotou, 2007). Various agricultural wastes were investigated for preparation of activated carbon. These include various parts of the fruits and cereals that are used for making activated carbons, such as peanut pods, stone of apricot, spent tea leaves, peels of orange, cherry stones, mango peel and stones, almonds, rice husk, rice bran, corn cobs, wood, wheat barn, wheat husks, sugarcane bagasse etc (Bhatnagar and Sillanpaa, 2010).

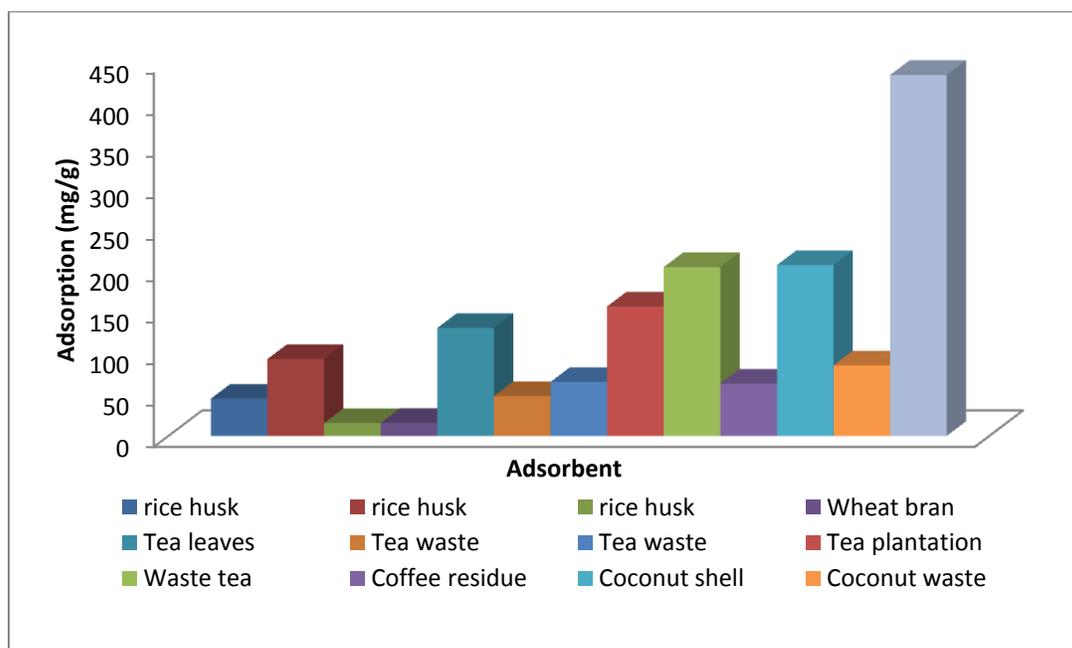


Figure 1.3. Graphical representation of some agricultural waste and their maximum adsorption capacity

Activated carbon synthesized from these materials can be used to remove a wide variety of pollutants such as, heavy metals, volatile organic compounds, pesticides and dyes coming out from industrial and agricultural facilities. These materials are used successfully and efficiently for removal of phenol and its derivatives such as *p*-cresol.

Adsorption of *p*-cresol

Previous researchers have studied the adsorption of *p*-cresol using various sources of activated carbons. Singh et al. (2008) used a carbonaceous agricultural waste *Parthenium*

hysterophorous by activating it chemically with concentrated H_2SO_4 . BET surface area was found to be $260 \text{ m}^2 \cdot \text{g}^{-1}$. Maximum adsorption capacity was found at pH 6.0 which could remove $500 \text{ mg} \cdot \text{L}^{-1}$ of *p*-cresol. Adsorption followed pseudo-first order kinetics. Effect of pH on adsorption revealed that adsorption increased from pH 3 to 6 but adsorption decreased for pH greater than 7. Effect of adsorbent dose on adsorption of *p*-cresol was investigated with varying amount of $1\text{-}20 \text{ g} \cdot \text{L}^{-1}$ of parthenium based activated carbon (PAC) where as initial concentration, temperature, and pH of solution were kept constant at $500 \text{ mg} \cdot \text{L}^{-1}$, $28 \text{ }^\circ\text{C}$ and 6 respectively. After maximum removal of 99%, effect of adsorption dose was insignificant. Initial *p*-cresol concentration was varied from 100 to $1000 \text{ mg} \cdot \text{L}^{-1}$ where as temperature, pH and adsorbent dose were held constant at $28 \text{ }^\circ\text{C}$, 6, and $10 \text{ g} \cdot \text{L}^{-1}$ respectively, to study the effect of adsorption. It was found that at a constant adsorbent dose, adsorption decreased with increase in *p*-cresol concentration.

Huang, (2009) studied adsorption of phenol and *p*-cresol by a carbonylated hypercrosslinked polymeric adsorbent. Adsorption capacity for *p*-cresol was found to be $141.5 \text{ mg} \cdot \text{g}^{-1}$ and that of phenol was $80.52 \text{ mg} \cdot \text{g}^{-1}$ at equilibrium concentration of $100 \text{ mg} \cdot \text{L}^{-1}$ and temperature of 293K . Adsorption capacity of *p*-cresol was larger than phenol due to lower solubility of *p*-cresol in water. Adsorption isotherm data fit well to Langmuir model and kinetics followed pseudo-second-order rate equation. Adsorption showed stability in acidic and neutral pH. NaCl and Cd^{2+} exhibited positive and negative adsorption effect. Adsorption mechanism was proposed by pore filling and hydrophobic interaction.

Hadjar et al., (2011) used a mixture of novel diatomite/carbon composites and carbon charcoal for adsorption of *p*-cresol. With a surface area of 100 and 400 m² g⁻¹, they exhibited adsorption of 29 and 82 mg.g⁻¹. Adsorption kinetics followed pseudo-second-order rate equation where as adsorption isotherm fitted well to Langmuir model. Study on effect of pH revealed that amount adsorbed was constant in the pH range of 2-10. Amount of adsorption increased with increase in carbon content. In this work it was inferred that adsorption of *p*-cresol was governed by hydrophobic character of the adsorbent and abundance of open porous structure.

Daifullah and Girgis (1998) studied adsorption of phenol derivatives by using apricot stone shells. Activated carbon from the apricot stone shells were synthesized by impregnating with H₃PO₄ and then carbonized at 300-500 °C. Seven phenolic compounds were used for adsorption: phenol, *m*-cresol, *p*-cresol, 2-chlorophenol, 4-nitrophenol, 2,4-dichlorophenol, and 2,4-dinitrophenol. Maximum adsorption capacity of *p*-cresol was determined to be 107.85 mg.g⁻¹. Adsorption capacity of *p*-cresol was affected by porosity of the carbon and molecular dimension of the sorbates. It was found that uptake was inversely proportional to solubility and isoelectric point.

Ravi et al., (1998) illustrated adsorption of phenol, cresol isomers and benzyl alcohol onto activated carbon at different temperatures. Adsorption was performed at three different temperatures, 278, 298 and 323 K which indicated chemisorption or adsorption in micropores. Adsorption isotherms were fitted well to Langmuir model. Adsorption increased with increase in temperature from 278 to 298 K where as it decreased with temperature from

298 to 323 K. Desorption study showed an irreversible adsorption on the carbon surface at lower concentrations.

Nouri et al., (2001) did a comparison study of adsorption capacity of *p*-cresol and *p*-nitrophenol onto activated carbon in single and double solute. Adsorption was formed at pH 2, 8, 10 and 12 which inferred that adsorption was higher at pH greater than 8. This is because of the basic nature of *p*-cresol which in acidic condition becomes positively charged leading to lower uptake. Similarly at higher pH of 12, *p*-cresol is in ionic form as it is above its pK_a (10.6) which decreases uptake amount. Presence of more than one solute decreased the maximum adsorption capacity and the adsorption affinity of carbon for the principal compound.

Despite so much research on phenol and its derivatives. The actual mechanism that is responsible for adsorption is still unknown. All the above researchers have studied individually different factors responsible for adsorption but interaction effects due to these factors are unknown. This research is focused on synthesizing low cost adsorbent and study of interaction of different factors of adsorption.

Hypothesis

1. *p*-cresol due to its electron donating methyl and hydroxyl groups, so for its adsorption a basic carbon is needed.
2. Presence of surface oxygen will inhibit adsorption of *p*-cresol.

Objectives

For efficient removal of *p*-cresol from cost effective stand point, adsorbents should be synthesized from low cost precursor. In addition to the physical variables (like temperature, pH, agitation), other factors also play a role in adsorption of *p*-cresol, but very limited studies have been done on the interaction between adsorbent surface and the adsorbate which also influences adsorption. Hence, this research was divided into two phases. In the first phase, preliminary experiments were performed using a commercial activated carbon. Effects of pH, temperature, and adsorbent dose were studied. In addition, the role of surface acidity on adsorption was also investigated. The results obtained in the first phase were used as a guideline to synthesize a low-cost adsorbent that was studied in the second phase of this project. Specifically, this thesis focused on: the following objectives:

1. Synthesize low-cost pine wood activated carbon (PAC) by optimizing carbonization time, impregnation ratio (IR), and carbonization temperature.
2. Characterize the PAC.
3. Study adsorption kinetics and isotherms.
4. Determine the effect of 2-methylbutrylaldehyde on adsorption of *p*-cresol.
5. Confirm the role of dissolved and surface oxygen on adsorption of *p*-cresol

Results from this research will help in synthesizing low cost adsorbents and it will demonstrate the mechanism involved in the adsorption of *p*-cresol. Based on the data collected and inference from the surface chemistry and kinetics for this activated carbon, it can be used for removal of *p*-cresol in a larger scale in swine lagoon.

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CHAPTER TWO

Adsorption of *p*-cresol on Granular Activated Carbon

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ABSTRACT

Swine farming emits several odorous volatile organic compounds, one of which is *p*-cresol (4-methylphenol). Considering the layout of a swine farm, adsorption is one of the most suitable technologies for mitigating organic pollutants. In this study, commercial granular activated carbon (GAC) was tested as an adsorbent for removing *p*-cresol from aqueous solution. Batch experiments with GAC were performed to assess the combined effects of temperature (15-35°C), pH (6-8), and adsorbent dose (10-30 g L⁻¹) on adsorption of *p*-cresol. The results indicated that adsorption capacity of *p*-cresol decreased with increasing adsorbent dose, whereas the effects of pH and temperature were not significant. Optimum adsorption capacity of 12.02 mg g⁻¹ was observed at temperature of 25° C, pH of 7, and adsorbent dose of 3.2 g L⁻¹. It was also found that presence of isovaleric acid and formaldehyde enhanced adsorption of *p*-cresol. Kinetic analyses indicated that *p*-cresol adsorbed mainly via chemisorption and adsorption was limited mainly via intra-particle diffusion. The role of solvent was not significant suggesting that water did not compete with *p*-cresol. Furthermore, surface oxygen somewhat inhibited adsorption of *p*-cresol perhaps due to enhancement of hydrophilicity. It is proposed that adsorption occurred mainly via electron-transfer between *p*-cresol and activated carbon. Sample design calculations are also presented to aid the swine producers to estimate the carbon dosage. Our data suggests that adsorption could effectively mitigate *p*-cresol released from swine facilities.

Keywords: Adsorption; *p*-cresol; Activated carbon; Kinetics; Isotherms; RSM, USA

1. Introduction

Swine farming operations typically store manure, urine, and spilled feed in pits before transferring the waste materials to an anaerobic lagoon. During storage, these waste materials are microbiologically decomposed into ammonia and malodorous volatile organic compounds such as *p*-cresol (4-methylphenol). Toxicity and adverse effect of *p*-cresols on human skin, eyes, and respiratory track can be felt even at very low concentrations due to which the United States Environmental Protection Agency has categorized *p*-cresol as priority pollutant (US-EPA, 1999).

P-cresol is a positional isomer of phenol. Various physical, chemical and biological processes have been used for removal of phenol and other pollutants from wastewater such as membrane filtration, advanced oxidation, electrolysis, activated sludge and adsorption (Mohd Din et al., 2009), most of which are not practical for use in swine operations. However, adsorption is most versatile due to high efficiency, simplicity in design, and operation (Allen et al., 2005a). Adsorption is a process in which certain surfaces attract specific compounds (pollutants) due to the physical and chemical interaction between the surface and the pollutants (Dabrowski, 2001). Due to large surface area, porous structure, and favorable chemistry, activated carbon and other similar materials has been extensively tested as adsorbent for removing water pollutants such as phenols by several groups of researchers (Dabrowski, 2001; Rodrigues et al., 2011; Ahmad et al., 2009; Hameed and Rahman, 2008).

There are several reports in the literature on adsorption of *p*-cresol on activated carbons. For example, adsorption of *p*-cresol using a parthenium- based activated carbon was reported by Singh et al. (2008). Their study suggested pH in the range of 3-7 did not have a significant effect on adsorption where adsorption increased with adsorbent dose. Huang (2009) evaluated carbonylated hypercrosslinked polymeric adsorbent for adsorption of phenol and *p*-cresol and found that adsorption was effective when pH was less than 8. Similarly, Hadjar et al. (2011) showed that adsorption of *p*-cresol on a novel diatomite/carbon composite was effective in a pH range of 2-10. Recently, Kilic et al. (2011) tested tobacco residues for removal of phenol. The authors found that phenol adsorption decreased with increase in temperature from 20 to 50° C. For optimal design of adsorption systems, quantitative information on combined effect of lagoon temperature, pH, and adsorption capacities are needed. In addition, lagoon liquid contains several organic compounds such as volatile fatty acids, aldehydes, indoles, and presence may influence adsorption of *p*-cresol. Hence in this research, we focused on: 1) determining the combined effect of temperature, pH, and adsorbent dose on adsorption, (2) investigating the effect of volatile fatty acids and aldehydes on adsorption of *p*-cresol, (3) determining adsorption kinetics and isotherms, (4) studying the effect of solvent on adsorption, (5) proposing a possible mechanism of adsorption.

2. MATERIALS AND METHODS

2.1 Materials

Commercial granular activated carbon derived from coconut shell (GAC) (C 270C, Fisher Scientific, Inc.) was tested as an adsorbent. Analytical grade *p*-cresol (99% purity, ACROS Organics), methanol, formaldehyde, isovaleric acid (IVA), and hexane (Fisher Scientific, Inc.) were used without any further modification.

2.2 Experimental Design

A central composite design (CCD) similar to that of Kalavathy et al. (2009), Singh et al. (2011) and Sahu et al. (2009) was used. In this research effects of temperature, pH and adsorbent dose were studied. Levels for these factors were selected based on the typical conditions prevailing in swine lagoons, i.e., temperature of 15-35° C and pH of 6-8. From an economic standpoint, an adsorbent dosage of 10-30 g L⁻¹ was selected.

The design consisted of 2³ factorial levels and 2×3 axial levels and 6 center points. The factorial points, coded +1 and -1 in Table 1 comprised of an unreplicated 2×2×2 complete factorial design and the axial points augment this design with more extreme levels (denoted α in Table 2.1).

Table 2.1. Experimental factors and their coded levels of independent variables for central composite design.

Factors	Code	Coded variable levels				
		$-\alpha$	-1	0	1	$+\alpha$
Temperature ($^{\circ}$ C)	X ₁	8.18	15	25	35	41.82
Adsorbent dose (g L ⁻¹)	X ₂	3	10	20	30	36.8
pH	X ₃	5.32	6	7	8	8.68

The axial points, where two factors set to the center levels (coded 0) and the third set to a level more extreme than the factorial points, enable estimation of nonlinear dependencies of adsorption on adsorption dose, pH, and temperature. The levels of the axial points, coded $+\alpha$ and $\alpha = 1.682$, were chosen so that design is rotatable. This means that the variance of the estimated adsorption at any configuration of the three experimental factors depended only on the distance of the configuration from the center points (Ahmad et al., 2009).

Center points were added to enable estimation of experimental error variance and test for lack of fit of the quadratic regression model. In all, there were 8 factorial points, 6 axial points and 6 center points, for a total of 20 observations per response variable. The experimental sequence was randomized to minimize the effects of uncontrolled errors. The data obtained was used to develop an empirical model to correlate the adsorption of *p*-cresol

with the temperature (X1), adsorbent dose (X2), and pH (X3) using a second degree polynomial equation as given below:

$$\hat{Y} = \beta_0 + \sum_i^n \beta_i x_i + \sum_{ii}^n \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i x_j \quad (1)$$

where \hat{Y} is the response, β_0 is the intercept, β_i the linear coefficients, β_{ii} the interaction coefficients, β_{ij} the quadratic coefficients and x_i, x_j are the coded values of *p*-cresol adsorption variables.

2.3 Batch Adsorption

All experiments were performed in 150-mL serum using 100 mg L⁻¹ of *p*-cresol solution. The pH of the solution was adjusted using 0.1N H₂SO₄ and diluted NaOH. Subsequently, 100 mL of *p*-cresol solution was mixed a predetermined amount of activated carbon in 150 mL serum bottles placed on a hot plate. The contents in the serum bottles were agitated at 450 rpm via a magnetic stirrer. As adsorption progressed, liquid samples were drawn periodically (0.5 mL every 3 min) using a micropipette and analyzed for *p*-cresol concentration using a gas chromatograph equipped with a mass selective detector (GC-MS) (Agilent Technologies, 7890 A) and a HP-5 MS column (30 m x 0.25 mm x 0.25µm). Data was acquired using an oven temperature of 105° C to 185° C @ 20° C min⁻¹ and a split ratio of 150:1 (1.2 mL min⁻¹) while injector and detector were maintained at 250° C.

From the concentration data obtained from GC-MS, adsorption of *p*-cresol was calculated by the following equation:

$$q_t = \frac{(c_0 - c_t) \times v}{w} \quad (2)$$

where q_t (mg g^{-1}) is the adsorption capacity, c_0 and c_t (mg L^{-1}) are the liquid-phase concentrations of *p*-cresol at the beginning ($t=0$) and at equilibrium time t respectively, v is the volume of solution (L) and w is the mass of the activated carbon (g).

All experiments were performed in duplicates and mean concentrations and standard error of the mean were used for plotting.

2.4 Effect of Volatile Fatty Acids and Aldehydes on Adsorption of *p*-cresol

Separate experiments in duplicates were performed to determine the effect of volatile fatty acids and aldehydes on adsorption of *p*-cresol. Isovaleric acid (IVA) and formaldehyde were used as representative VOCs as they are expected to be found in swine lagoons. A mixture of *p*-cresol (1000 mg L^{-1}), IVA (1000 mg L^{-1}), and formaldehyde (1000 mg L^{-1}) (with traces of methanol) in DI water was prepared and mixed with 2 g of activated carbon. Samples were drawn periodically and analyzed for change in concentration.

2.5 Adsorption Kinetics and Isotherms

To determine the adsorption rate constants and mechanism of the *p*-cresol adsorption processes, data were analyzed using pseudo-first order (equation 3), pseudo-second order (equation 4), Elovich (equation 5) and intra-particle diffusion models (equation 6). Selection of the order of reaction was based on the value of correlation coefficients (R^2) as described by (Kilic et al., 2011; Demribas et al., 2004; Aravindhan et al., 2009).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

$$q_t = k_p t^{1/2} + C \quad (6)$$

In equations 3 through 6, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption capacity of *p*-cresol at equilibrium and at any given time t (min) and k_1 (min^{-1}) and k_2 ($\text{mg g}^{-1} \text{min}^{-1}$) 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 ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are the initial adsorption rate and desorption constants. K_p is intra-particle diffusion constant and C is a constant. In addition, to understand the effect of *p*-cresol concentration on adsorption capacity of GAC at a given temperature, Langmuir, (1916) (equation 7) and Freundlich, (1906) (equation 8) isotherm models were tested as shown below.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (7)$$

$$q_e = K_F C_e^{1/n} \quad (8)$$

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 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. K_F (mg g^{-1}) (mg L^{-1}) $^{-1/n}$ and n are adsorption capacity and Freundlich's adsorption constant respectively.

In addition, to determine the extent of physisorption and chemisorption, separate batch experiments similar to studies conducted by Rodrigues et al. (2011) were conducted using DI water and hexane (as desorbing agents) and spent GAC from previous experiments.

Typically, after attaining equilibrium, the GAC was separated from the solution via filtration. Subsequently, spent samples of GAC were mixed with DI water (and hexane) and agitated at 450 rpm at 25° C for 15 min. Liquid samples were collected periodically and analyzed for *p*-cresol concentration.

2.6 Effect of Solvent on Adsorption

To separate out the effect of water on adsorption of *p*-cresol, additional experiments in duplicate were performed using methanol and hexane as solvents. Typically, 100 mg L^{-1} solution of *p*-cresol was prepared using hexane, methanol, and water (for comparison) and

mixed with 2 g of GAC at 25° C (without any pH adjustment). Samples were collected periodically via a micropipette and analyzed for *p*-cresol concentration.

2.7 Possible Mechanism of Adsorption

To confirm the mechanism of adsorption, especially the role of surface oxygen groups, additional experiments were performed. Prior to that, the surface of the activated carbon was modified by treating with concentrated H₂SO₄ for 8 h to increase the oxygen content on the activated carbon surface. Subsequently, the acid treated activated carbon (GACA) was washed with DI water for 40 min to remove traces of any acid. Batch adsorption experiments were performed using GAC and GACA by mixing 2 g of adsorbent was mixed with 100 mL of *p*-cresol solution (200 mg L⁻¹) at 25° C without any pH adjustment. Samples were drawn periodically via a micropipette and analyzed for concentration of *p*-cresol using a GC-MS. In addition, GAC and GACA were characterized by determining the specific surface area (SSA), X-ray photoelectron spectroscopy (XPS), and acid value as described by Love et al. (2011).

3. RESULTS AND DISCUSSIONS

3.1 Development of model equation

Using the data collected in the CCD, a second order polynomial model was developed to describe the dependence of adsorption on temperature, adsorbent dose, and pH. The model was fitted using statistical software package JMP 9.0 (SAS, Cary, NC) and Design-Expert

7.0 (Minneapolis, MN). Table 2.2 shows the complete design matrix, actual, and predicted responses. Adsorption was found to be in the range of 2.62 to 12.02 mg g⁻¹. A quadratic regression model was suggested and the estimated model for adsorption of *p*-cresol in terms of coded value is given in eq (9).

$$\begin{aligned} \hat{Y} = & 4.8650 + 0.1697 X_1 - 2.3107X_2 + 0.0881X_3 - 0.2312X_1^2 + 0.7601X_2^2 \\ & - 0.1056X_3^2 - 0.3306X_1X_2 + 0.0451X_1X_3 \\ & - 0.0892X_2X_3 \end{aligned} \quad (9)$$

where X_1 , X_2 and X_3 are temperature, adsorbent dose, and pH respectively. The coefficients with one factor (X_1, X_2, X_3) represent the effect of one factor, while the coefficients with two factors (X_1X_2, X_1X_3, X_2X_3) and those with second-order terms (X_1^2, X_2^2, X_3^2) represent the interaction between the two factors and quadratic effect respectively. The positive sign indicates synergistic effect, while negative sign indicates antagonistic effect (Ahmad et al., 2009).

Table 2.2. Central composite design matrix

Run	X ₁ :Temp. code	X ₂ : Adsorbent dose code	X ₃ : pH code	Temperature (°C)	Adsorbent dose (g)	pH	Adsorption (actual) (mg g ⁻¹)	Adsorption Predicted (mg g ⁻¹)
1	-1	-1	-1	15	1	6	6.40±0.37	6.97
2	1	-1	-1	35	1	6	7.28±0.47	7.88
3	-1	1	-1	15	3	6	3.06±1.41	3.18
4	1	1	-1	35	3	6	3.09±0.59	2.77
5	-1	-1	1	15	1	8	6.48±0.87	7.23
6	1	-1	1	35	1	8	8.00±0.78	8.32
7	-1	1	1	15	3	8	3.24±1.09	3.09
8	1	1	1	35	3	8	2.98±0.62	2.86
9	-1.682	0	0	8.182	2	7	4.48±0.84	3.92
10	1.682	0	0	41.818	2	7	4.57±0.32	4.50
11	0	-1.682	0	25	0.318	7	12.02±0.43	10.90
12	0	1.682	0	25	3.682	7	2.64±0.90	3.13
13	0	0	-1.682	25	2	5.318	4.78±0.69	4.42
14	0	0	1.682	25	2	8.681	4.98±0.22	4.71
15	0	0	0	25	2	7	4.52±0.40	4.87
16	0	0	0	25	2	7	4.76±0.19	4.87
17	0	0	0	25	2	7	5.12±0.28	4.87
18	0	0	0	25	2	7	4.95±0.30	4.87
19	0	0	0	25	2	7	4.62±0.25	4.87
20	0	0	0	25	2	7	5.11±0.16	4.87

Analysis of data indicated that neither temperature (15-25 °C) nor pH (6-8) had any effect on adsorption. In addition, most of the variability in adsorption was explained by adsorbent dose, and there was evidence that the dependence is nonlinear. While the model explained most of the variability ($R^2=0.96$), there was a modest lack-of-fit, possibly because of modest departure from quadratic dependence on adsorbent dose.

3.2 Effect of temperature

Fig. 2.1 A and B show the interactive effect of temperature with adsorbent dose and pH on adsorption of *p*-cresol. Temperature did not seem to have any effect on adsorption capacity of GAC ($p=0.3340$). Our results are different than those reported by Ravi et al. (1998) who found that adsorption increased with increase in temperature from 5° C to 25° C and then decreased from 25° C to 50° C. Similarly, Kilic et al. (2011) reported a decrease in adsorption with increase in temperature from 20° C to 50° C perhaps due to deformation in the active sites at higher temperatures. The temperature-independent behavior observed in our research is probably due to a very fast adsorption process. As the carbon used in this study was alkaline in nature it might have facilitated phenol adsorption at a faster rate (around 40% of the *p*-cresol was adsorbed in 3 min).

3.3 Effect of pH

The solution pH is a major factor controlling adsorption rate of adsorption as it controls the surface charge on the activated carbon and adsorbate. *p*-cresol is more basic in nature due its electron donating methyl and hydroxyl groups (Singh et al., 2008). Combined effects of pH

with temperature and adsorbent doses are illustrated in Fig. 2.1 A and C respectively. The effect on adsorption due to pH and adsorption dose is shown in Fig. 2.1 B, which indicates that adsorption is independent of pH ($p=0.6096$) in the range of 6-8 which suggests that *p*-cresol was adsorbed in its neutral form ($pK_a \sim 10.2$). This is in good agreement with the results previously reported (Singh et al., 2008; Hadjar et al., 2011; Nouri et al., 2002). These studies reported that pH in the range of 2-10 has constant adsorption rate perhaps due to repulsion between the negatively charged adsorbent and negatively charged *p*-cresol at pH higher than pK_a . Similarly under highly acidic conditions, *p*-cresol becomes positively charged leading to an electrostatic repulsion between the adsorbent and adsorbate, which might have reduced the adsorption rate.

3.4 Effect of adsorbent dose

The combined effect of adsorption dose and temperature, adsorption dose and pH are shown in Fig. 2.1 B and C respectively. It is evident that temperature and pH are not playing roles in adsorption in comparison with the adsorption dose ($p=0.0001$). Adsorption increases with decrease in adsorbent dose, this observation can be understood as increase in number of adsorption sites with increase in adsorbent dose, which against a constant solution concentration would lower the concentration gradient in the bulk phase and the surface of the activated carbon, declining the rate of adsorption. In case of lower adsorbent dose the concentration gradient would be relatively high, resulting in higher adsorption rate. As

expected, adsorption capacity increased with decrease in adsorbent dose. These findings are in good agreement with results reported by Huang (2009) and Helen et al. (2009).

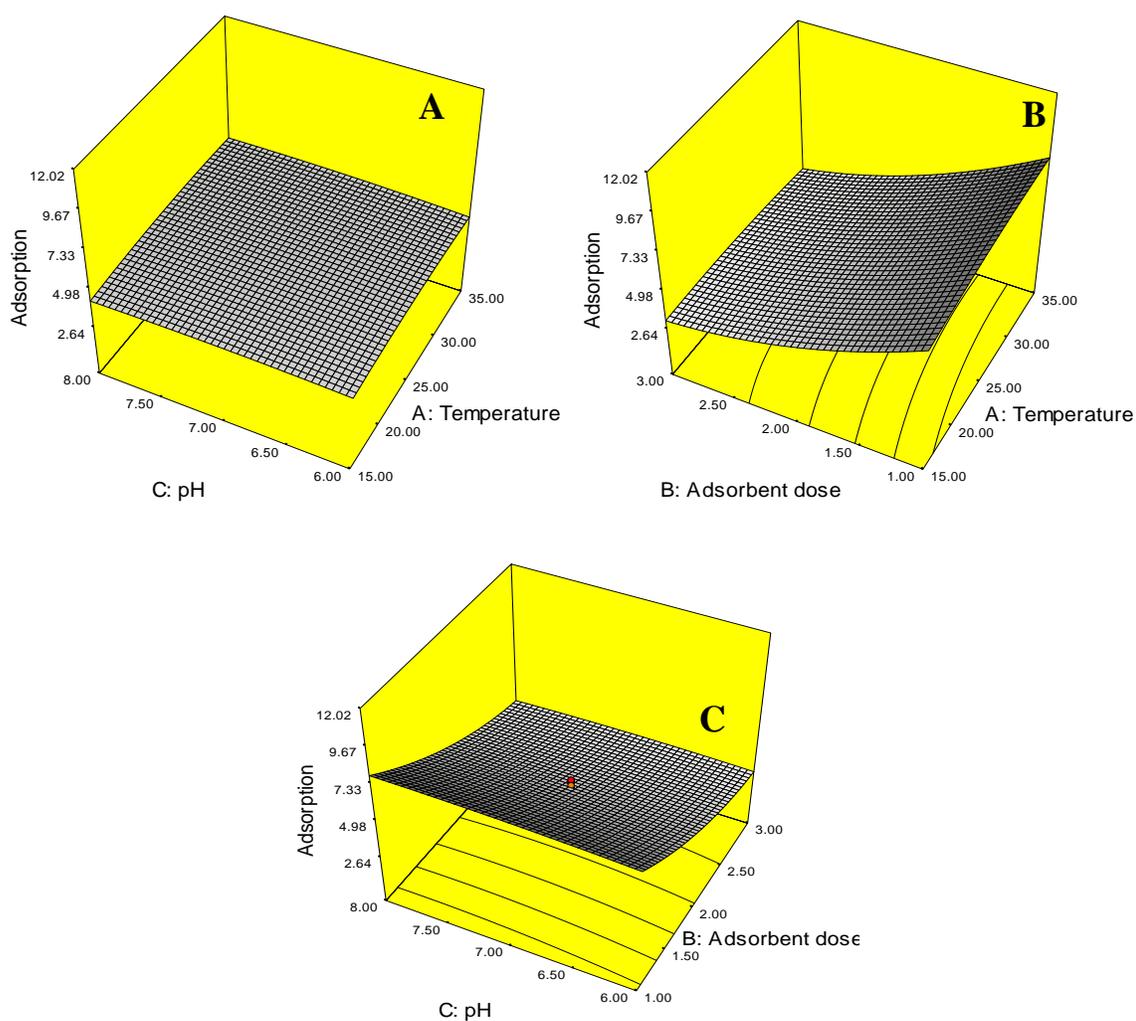


Figure 2.1. Surface plots of adsorption of *p*-cresol to describe combined effects of (A) Effect of pH and temperature, (B) adsorbent dose and temperature, and (C) pH and adsorbent

3.5 Optimization of *p*-cresol adsorption

The experimental conditions used to obtain data were optimized using JMP 9.0 (SAS, Cary, NC) and Design-Expert 7.0 (Minneapolis, MN). However a single solution could not be achieved as the solution was a saddle point, perhaps due to conservative ranges of the independent parameters (temperature, adsorbent dose and pH), which were based on the actual environmental conditions prevailing in swine lagoons. The lack of a single solution led to selection of a condition that has maximum adsorption capacity under more practical parameters. From the predicted model, a maximum adsorption of 10.90 mg g⁻¹ was obtained at temperature of 25° C, pH of 7 and adsorbent dose of 3.2 g L⁻¹. As temperature and pH had no effect on adsorption, aforementioned value was selected as the optimum. The experimental value for *p*-cresol adsorption under the same condition was found to be 12.02 mg g⁻¹, which is close to the optimized value (Table 2.2).

3.6 Effect of Volatile Fatty Acids and Aldehydes on Adsorption of *p*-cresol

Based on the reduction of *p*-cresol concentration in solution, adsorption of *p*-cresol increased significantly ($p = 0.005$) when 1000 mg L^{-1} each of IVA and formaldehyde were present in the mixture (Fig. 2.2). The increased adsorption of *p*-cresol may be attributed to favorable interaction between IVA and formaldehyde on carbon surface that resulted in additional active sites that were not available when only *p*-cresol was present. Nonetheless, this synergistic effect makes adsorption an effective option as several VOCs co-exist in a typical lagoon.

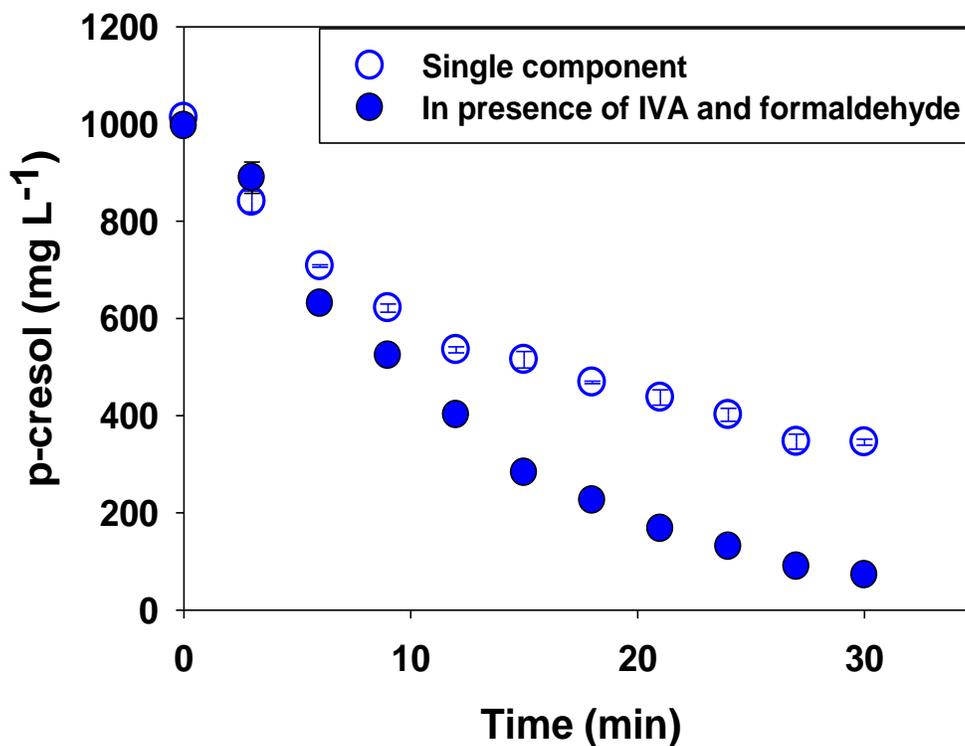


Figure 2.2. Effect of IVA and formaldehyde on adsorption of *p*-cresol on activated carbon ($n=2$). Experimental conditions: IVA, formaldehyde, and *p*-cresol = 1000 mg L⁻¹ each, Temperature = 25° C.

3.7 Adsorption isotherm

Adsorption of *p*-cresol at different temperatures is shown in Figure 3. The data were analyzed using Langmuir and Freundlich isotherm models via non-linear regression (SigmaPlot, Systat Software, Inc, San Jose, CA) and presented in Table 2.3. It appeared that the maximum adsorption capacity increased with temperature (15° C to 25° C) and decreased

as temperature of the system was further increased from 25° C to 35° C. Our observations were somewhat similar to that of Ravi et al. (1998) who found that adsorption increased with increase in temperature from 5° C to 25° C and then decreased from 25° C to 50° C. In addition, it is also evident that the experimental data does not conform to Langmuir's model at higher temperatures suggesting that the surface of the carbon was not homogeneous and interaction between the adsorbed substrate molecules were present. Other studies by Singh et al. (2008) and Hadjar et al. (2011) reported maximum adsorption capacities of 62.19 and 82 mg g⁻¹ with a surface area of 260 and 390 m²g⁻¹ respectively. Similarly Ayranci and Duman (2005) observed maximum adsorption capacity of 207.64 mg g⁻¹ and a surface area of 1464 m²g⁻¹, whereas Huang (2009) recorded maximum adsorption capacity 248.1 mg g⁻¹ with a surface area of 727 m²g⁻¹. In this study surface area was 662 m²g⁻¹ but maximum adsorption capacity was 68 mg g⁻¹ clearly suggesting that surface area and porosity did not influence uptake of *p*-cresol as was also observed by Daifullah and Gigris (1998).

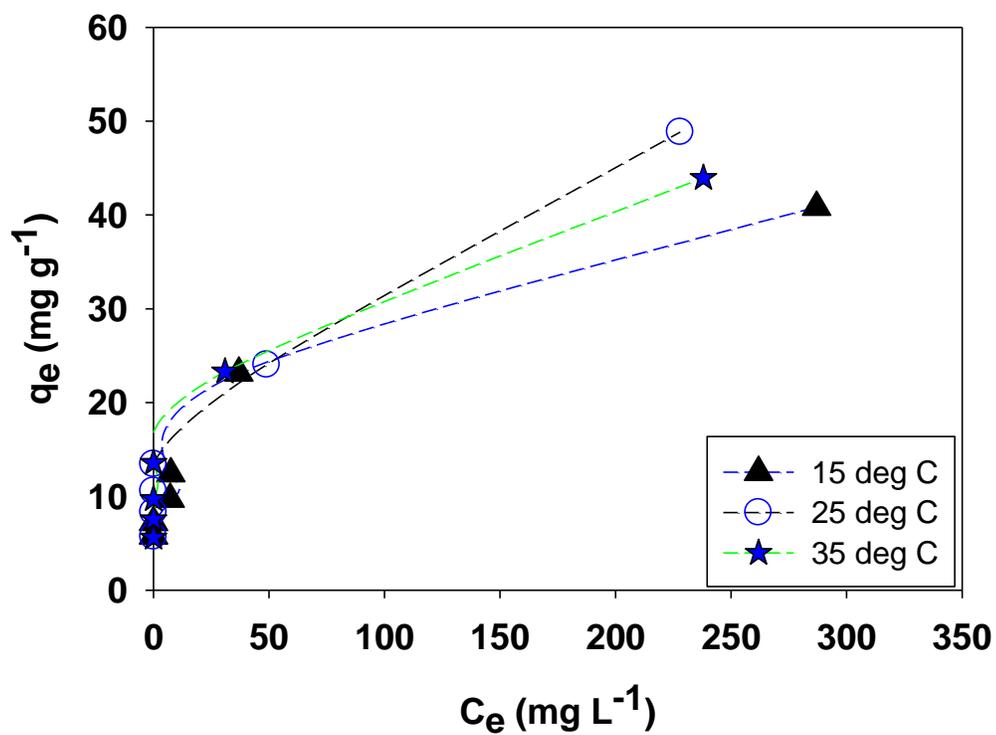


Figure 2.3. Adsorption isotherms of *p*-cresol at 15, 25, and 35 °C. Experimental conditions: pH: 5.8 and adsorbent dose: 2 g.

Table 2.3. Adsorption isotherm constants for *p*-cresol adsorption onto GAC.

Temp(°C)	Langmuir			Freundlich		
	Q ₀ (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K _F (mg g ⁻¹) (mg L ⁻¹) ^{-1/n}	1/n	R ²
15	43.7	0.038	0.89	6.25	0.33	0.89
25	68	0.01	0.69	3.99	0.46	0.7
35	52	0.02	0.65	8.0	0.31	0.65

3.8 Kinetics and mass transfer

Pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion model parameters were calculated using equation 3, 4, 5, and 6 respectively. Figure 2.4 A-D show representative plots of all the kinetic models fitted to the data. The kinetic parameters obtained from various models for the range of concentrations tested are shown in Table 2.4. Comparison of the average correlation coefficients indicated that pseudo-second order (average $R^2 = 0.89$) and Elovich (average $R^2 = 0.96$) models described the data better than pseudo-first order (average $R^2 = 0.73$) model. This implies that adsorption phenomenon is probably governed and limited by chemisorption (Tseng et al., 2003).

Allen et al. (2005b) and Cheung et al. (2007) described adsorption as a combination of external mass transfer to the adsorbent surface, followed by adsorption and diffusion of adsorbate into the porous matrix of the adsorbent. Figure 2.4 D shows the overall kinetic processes that were observed with GAC used in this study that included three linear zones. As explained by Cheung et al. (2007), the initial portion of the curves represented the external mass transfer. In our work, as expected, mass transfer rate increased (steeper slope) as concentration of *p*-cresol increased in the system. Additionally, as adsorption continued, the slope of the curves decreased suggesting the role of intra-particle diffusion (Allen et al., 2005c).

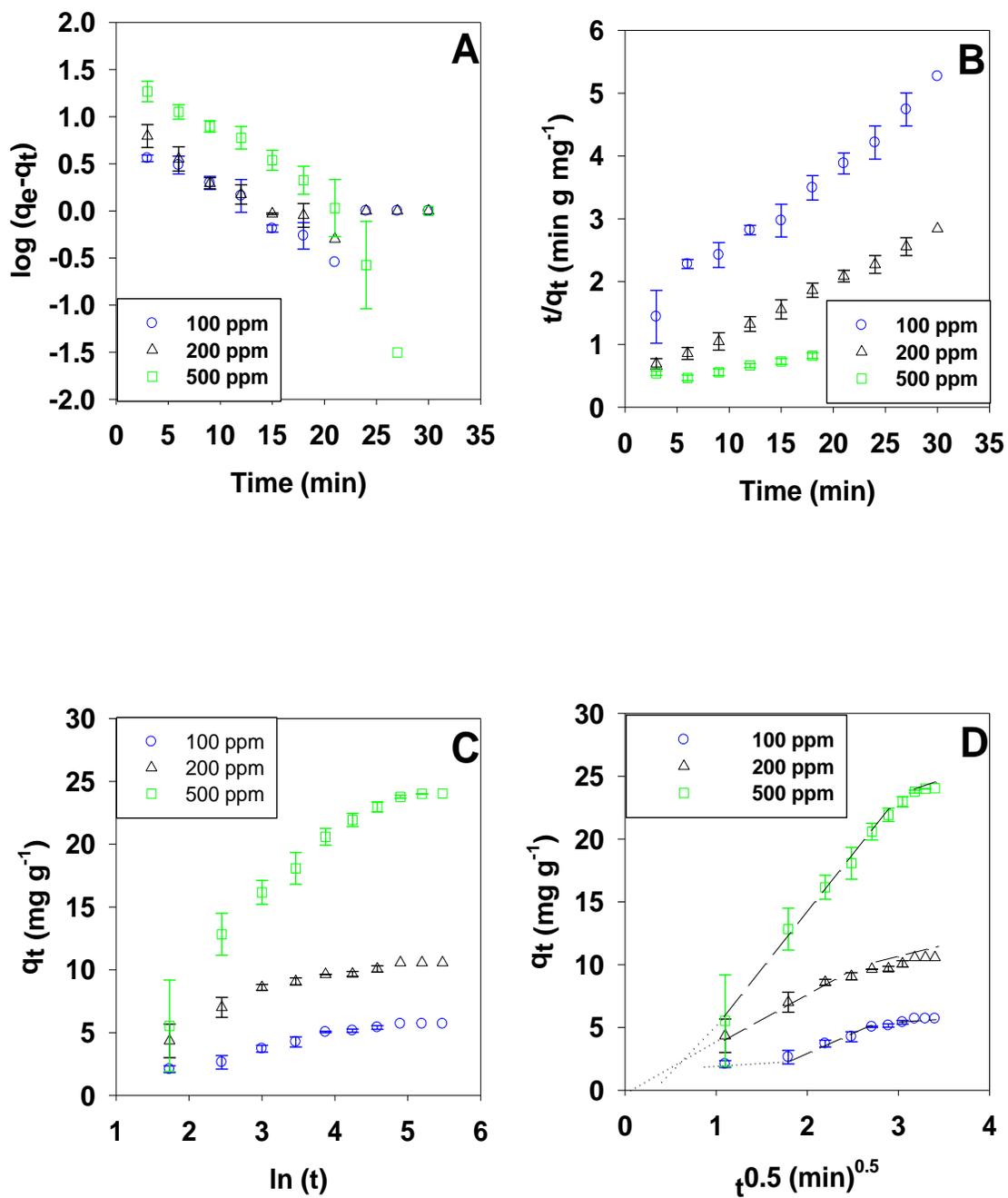


Figure 2.4. Representative kinetic plots for (A) I-order, (B) II-order, (C) Elovich, and (D) intra-particle diffusion models. Experimental conditions: Temperature: 25 °C, pH: 5.8, and adsorbent: 2 g.

The rate of adsorption decreased as *p*-cresol reached the mesopores and further decreased as the diffusional processes were limited perhaps due to smaller size of micropores than the size of *p*-cresol molecule (6.6 Å X 4.3 Å) (Huang, 2008). Further, the curves did not pass through the origin and hence it is expected that adsorption was somewhat limited by external and internal mass transfer effects although internal diffusion appeared to be substantially higher. The average intra-particle diffusion constant was found to be 2 which was smaller less than those reported by (Kilic et al., 2011; Hameed and Rahman, 2008) suggesting that intra-particle diffusion is the major rate-limiting step in adsorption of *p*-cresol on GAC.

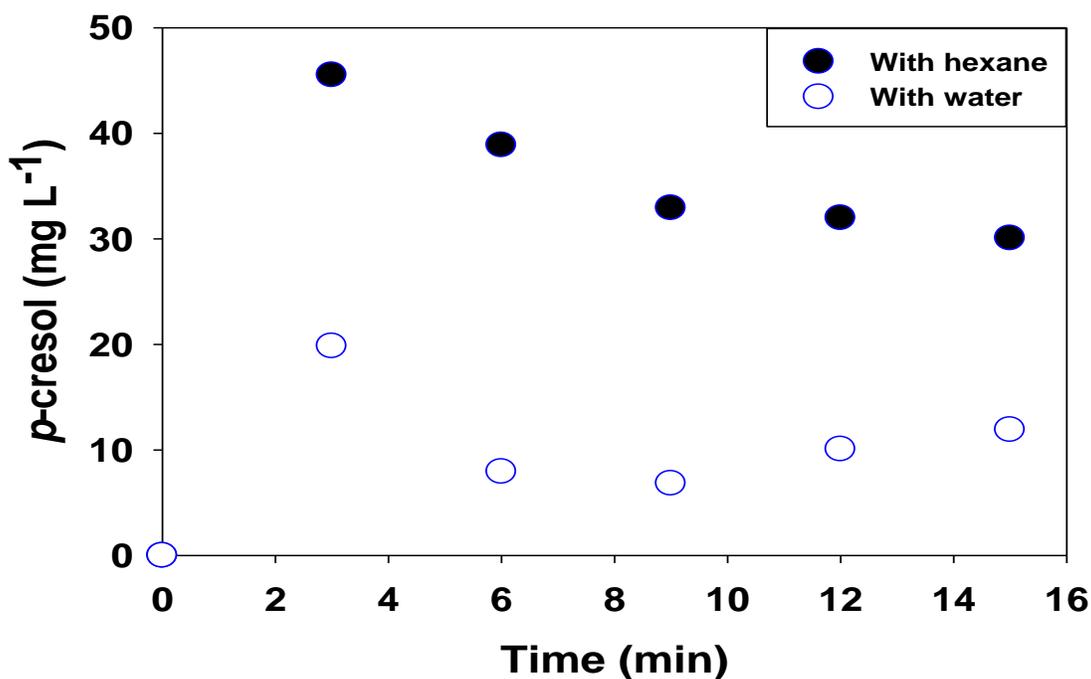


Figure 2.5. Desorption of *p*-cresol from GAC into water and hexane. Experimental conditions: Temperature: 25 °C, pH: 5.8, and adsorbent dosage: 2 g.

In addition, results from desorption experiments revealed that the desorption capacities of water and hexane for *p*-cresol adsorbed on GAC were significantly different ($p= 0.005$) (Figure 5). On average 9.45 mg L^{-1} and 29.89 mg L^{-1} of *p*-cresol was removed from the activated carbon using water and hexane respectively as desorbing agents. In both cases, some involvement of some physical adsorption was evident, but clearly chemisorption was the main mode of removal of *p*-cresol. Our findings are in good agreement with experimental data obtained by Rodrigues et al. (2011) who found that water has lower desorbing capacity than ethanol in desorbing phenol.

Table 2.4 Kinetic parameters for adsorption of *p*-cresol.

Experiment (Temp_Conc)	Pseudo 1 st order		Pseudo 2 nd order		Elovich			Intra-particle		
	R ²	k ₁ (min ⁻¹)	R ²	k ₂ (mg g ⁻¹ min ⁻¹)	R ²	α (mg ⁻¹ g min ⁻¹)	β (g mg ⁻¹)	R ²	k _p (mg g ⁻¹ min ^{-0.5})	c
15_100	0.808	0.090	0.977	0.042	0.984	1.718	0.599	0.948	1.045	0.594
15_200	0.730	0.128	0.965	0.020	0.989	2.163	0.352	0.970	1.782	0.738
15_500	0.974	0.120	0.008	2.5E-05	0.904	3.872	0.125	0.915	5.097	3.79
15_1000	0.827	0.101	0.010	1.7E-05	0.822	4.679	0.080	0.889	8.242	9.14
25_100	0.558	0.066	0.948	0.026	0.985	1.587	0.569	0.971	1.108	0.205
25_200	0.713	0.078	0.985	0.028	0.968	2.445	0.323	0.915	1.909	1.431
25_500	0.769	0.172	0.916	0.004	0.988	3.165	0.130	0.959	4.799	0.281
25_1000	0.970	0.142	0.890	0.001	0.980	3.997	0.064	0.980	9.812	1.631
35_100	0.479	0.046	0.978	0.050	0.964	1.769	0.592	0.906	1.04	0.696
35_200	0.582	0.071	0.988	0.036	0.961	2.459	0.354	0.901	1.745	1.514
35_500	0.854	0.149	0.972	0.008	0.985	3.065	0.141	0.949	4.394	1.92
35_1000	0.921	0.150	0.944	0.003	0.987	3.613	0.074	0.952	8.419	2.06

3.9 Effect of solvent

Effect of solvent on adsorption was studied by using water, methanol, and hexane as solvents in batch experiments at 25 °C and adsorbent dose of 2 g. It was found that there was no significant difference ($p=0.602$) (Figure 2.6) in adsorption suggesting that water molecules were not competing with *p*-cresol for the same active site during adsorption. Similar suggestions were made by Hadjar et al., (2011) who tested diatomite and charcoal-based adsorbents for mitigation of *p*-cresol. This non-dependence of solvent for adsorption of *p*-cresol by GAC makes it quite suitable for practical application in swine lagoons.

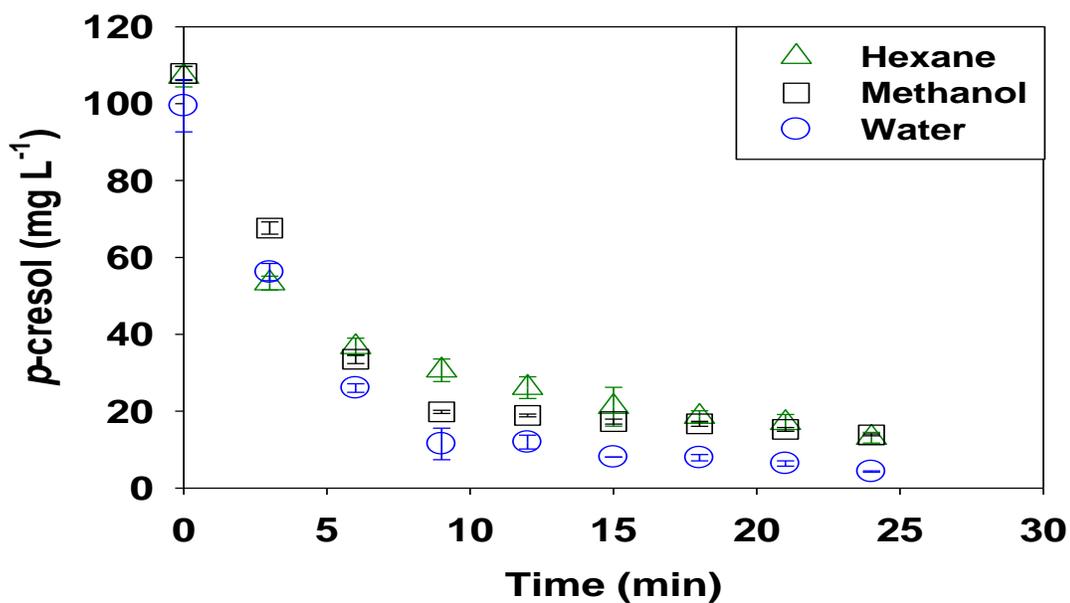


Figure 2.6. Effect of solvent on adsorption of *p*-cresol on GAC. Experimental conditions:

Temperature: 25 °C, pH: 5.8, and adsorbent dosage: 2 g.

3.10 Possible mechanism of adsorption

The Brunauer–Emett–Teller (BET) surface area of the GAC was found to be $662 \text{ m}^2 \text{ g}^{-1}$. However, after treatment with H_2SO_4 the surface area decreased to $159 \text{ m}^2 \text{ g}^{-1}$ suggesting that oxidation with sulfuric acid resulted in destruction of the pore structure of the carbon.

The spectra obtained from X-Ray photoelectron spectroscopy (XPS) analysis of GACA and GAC are shown in Fig. 2.7 A and B, respectively.

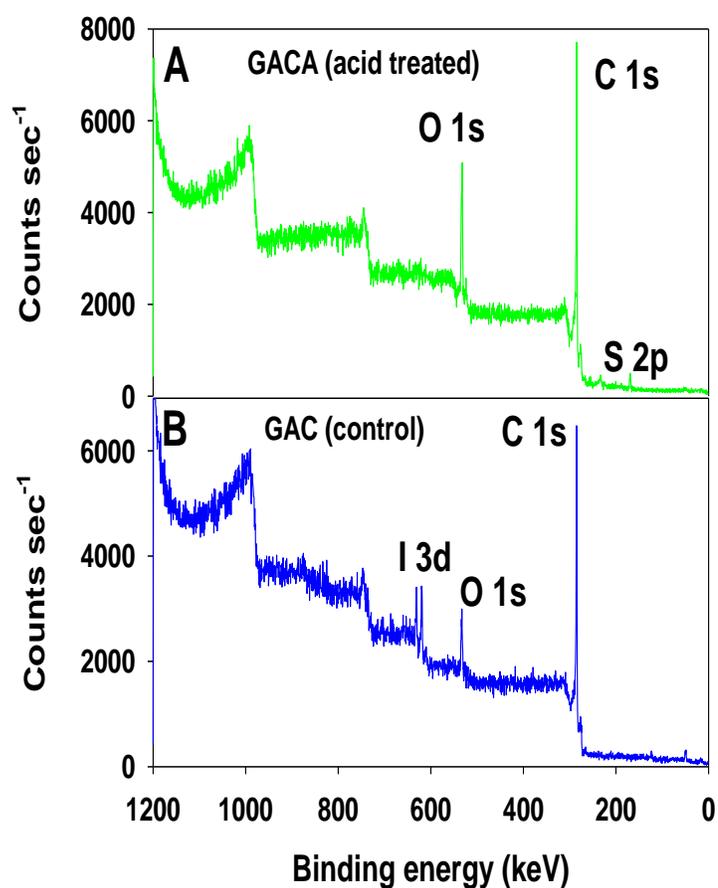


Figure 2.7. XPS spectra of GACA (A) and GAC (B).

The data showed significant increase (58%) in surface oxygen concentration (Fig 2.7 A) after acid treatment when compared to control (GAC, Fig 2.7 B). In addition, a small peak (S 2p) at 169 eV (Fig 2.7 A) confirmed the presence of sulfonic group most likely due to the reaction between sulfuric acid and carbon. Similar observations were reported by Gomes et al. (2011) who observed sulfonic groups at 170.4 eV. The increase in oxygen was also confirmed by the decrease in the acid values of GAC from 8.66 to 1.77 (Fig 2.8).

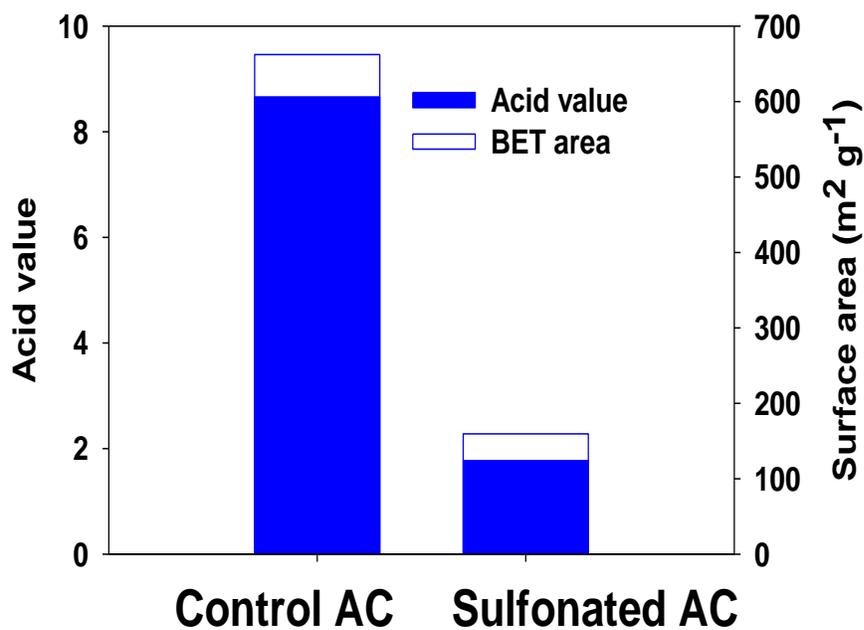


Figure 2.8. Acid value and specific surface area of GAC and GACA

When tested, adsorption capacity of GACA significantly decreased when compared to GAC ($p=0.0006$). Fig. 2.9 shows the comparison of removal of *p*-cresol by GAC and GACA. Decrease in adsorption for GACA may be explained by the presence of increased oxygen which may have hindered the adsorption of *p*-cresol, as also reported by Dabrowski et al. (2005). Several researchers including Moreno-Castilla et al. (1995), Moreno-Castilla (2004), and Liu et al. (2010) described that the basicity of carbon played an important role in adsorption of phenols. The basic groups on the carbon surface are expected to serve as electron donors to the phenolic rings thereby facilitating adsorption via electron transfer at oxygen deficient areas on the carbon. In our work, the treatment of surface with acid must have minimized the oxygen-deficient sites resulting in decrease in adsorption of *p*-cresol.

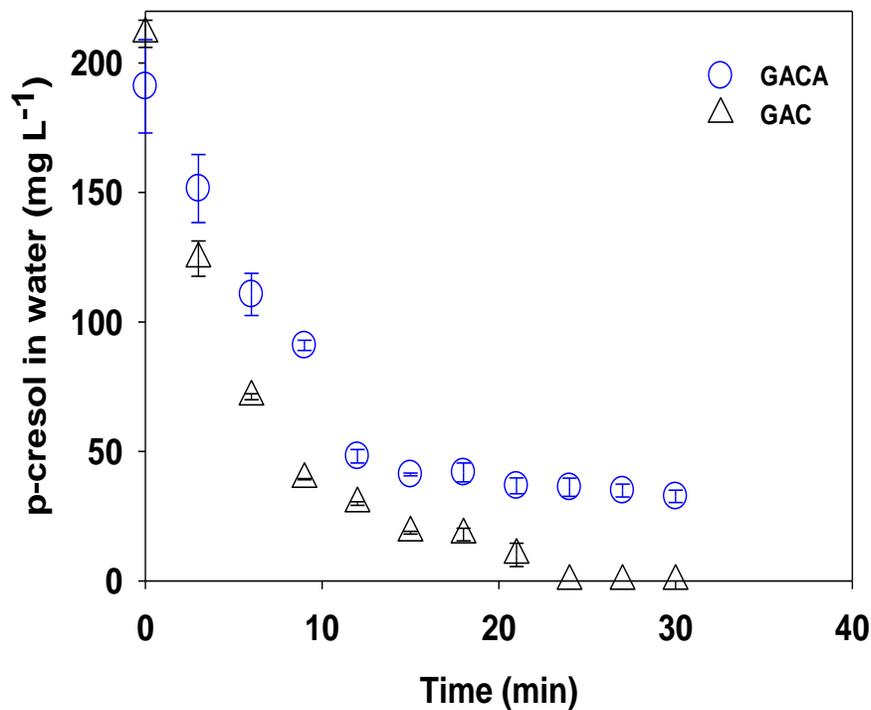


Figure 2.9. Adsorption of *p*-cresol on GAC and GACA. Experimental conditions:

Temperature: 25 °C, unadjusted pH, and adsorbent dosage: 20 g L⁻¹.

Terzyk (2003) proposed that the water tend to compete with phenols on hydrophilic surfaces. The acid treatment of activated carbon may have substantially increased the hydrophilic potential of the surface, which might also have contributed to reduction in adsorption capacity (Nabais et al. (2009). The authors Nabais et al. (2009) also observed that the adsorption capacities of nitric acid-oxidized activated carbons were lower than non-acid treated samples.

Multiple theories have been proposed to describe adsorption of phenols on activated carbon. Moreno-Castilla (2004), Rodriguez et al. (2011), Nabais et al. (2009), Dabrowski et al.

(2005), and others reviewed mechanisms originally described by Coughlin and Ezra (1968) and Mattson et al. (1969) and suggested that adsorption may proceed via combination of π - π interactions, hydrogen bonding, and electron transfer between phenols and activated carbon. In our work, we observed that GAC adsorbed 100% of *p*-cresol within 24 min. But within the same time, acid treated carbon (oxidized) (GACA) was still able to adsorb 81% of *p*-cresol suggesting that GACA was reasonably active despite oxidation treatment (acid value dropped from 8.66 to 1.77). Based on Coughlin and Ezra's (1968) proposition, oxidation of carbon is expected to remove electrons from the π band of the carbon and weaken the π - π interactions between *p*-cresol and GAC resulting in significant reduction in adsorption of *p*-cresol on GACA. Interestingly, in our work, GACA still retained 81% efficiency when compared to GAC (control) suggesting adsorption continued despite supposedly weakened π - π interactions.

Some authors including Coughlin and Ezra (1968) suggested that water selectively adsorbs on oxygen-rich functional groups thereby inhibiting adsorption of phenols on carbon surface. In our work, there was some evidence of reduced adsorption on acid-treated carbon. In other words, the competition between water and *p*-cresol may not be significant for untreated activated carbon that was used in this research. Additionally, our experiments with various solvents supported our proposition. When we tested activated carbon using hexane, methanol and water as solvents, the adsorption capacities were similar, which suggested that water molecules did not compete with phenol.

Mattson et al. (1969) on the other hand, hypothesized that adsorption of phenols proceed via an electron transfer between carbon surface and phenol with carbonyl groups acting as stronger electron donors than others. In addition, they hypothesized that adsorption is expected to continue to occur on the basal planes of the carbon. Our results are somewhat consistent with this explanation as we still observed substantial adsorption on GAC even after acid treatment.

3.11 Practical Implications and Design Calculations

The results obtained from this research suggests that adsorption is effective in mitigation of *p*-cresol from water under actual lagoon operating conditions. When compared to other treatment technologies such as biological filtration, adsorption is more practical and feasible. Typical lagoons contain millions of liters of liquid with daily addition of thousands of liters of manure and wastewater. Continuously treating such large quantities of water via biological filtration poses economic and operational challenges. Adsorption, on the other hand, involves no equipment and can still occur continuously *in-situ* until the carbon is saturated. Further, the spent carbon may be used as a soil amendment to enhance crop production or may be combusted or pyrolyzed for energy and chemical production.

In addition, design of adsorption systems is simple. As described by Cooney (1999), one can estimate the amount of carbon needed to adsorb a given amount of *p*-cresol relating the mass balance with isotherms. For instance, by combining equations 1 and 8 and the data presented in Table 3, one can estimate the mass of adsorbent needed for adsorption. For example, for a 1000-L mixed water system containing 100 mg L^{-1} of *p*-cresol at $15 \text{ }^{\circ}\text{C}$ that follows a Freundlich's model, the mass of adsorbent may be expressed as

$$W = \frac{(C_0 - C_t)}{6.25C^{(0.33)}} V \quad (10)$$

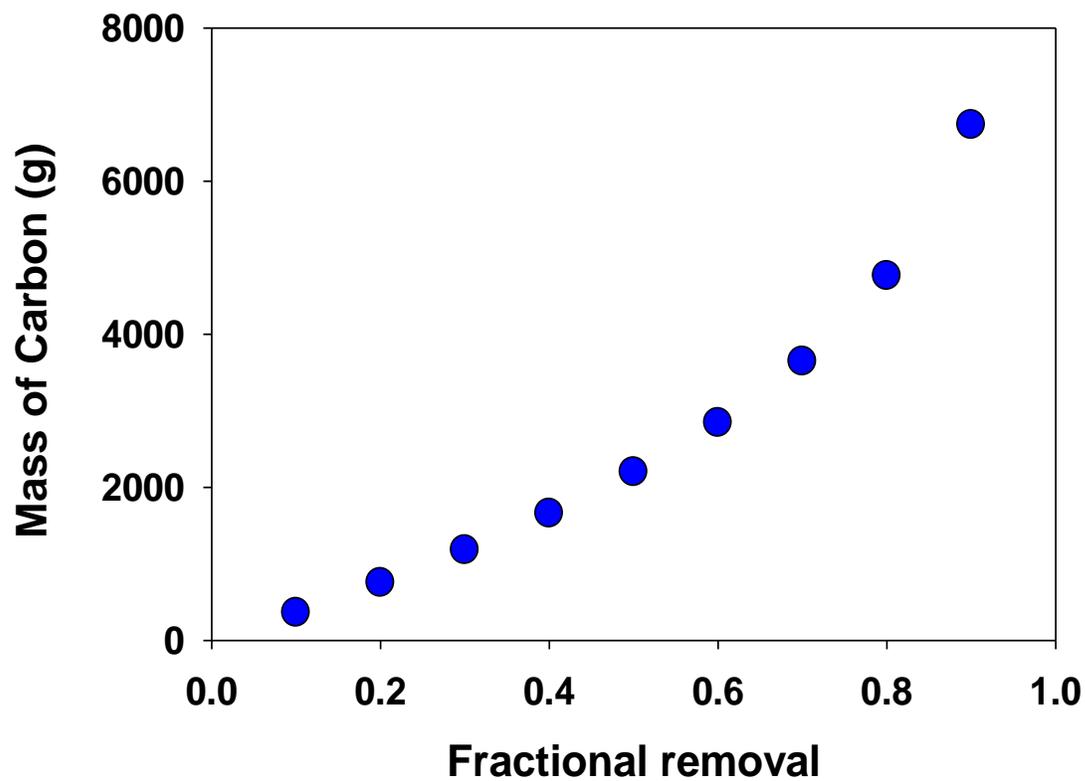


Figure 2.10. Simulated plot for estimation of adsorbent dosage for mitigation of p-cresol (100 mg L⁻¹)

By defining fractional removal, X as $\frac{C_0 - C_t}{C_t}$ and C_t as $C_0(1 - X)$ equation 10 may be expressed as

$$W = \frac{XVC_0}{6.25 [C_0(1-X)]^{0.33}} \quad (11)$$

where C_0 is the initial concentration of *p*-cresol (e.g., 100 mg L^{-1}), C_1 is the required final equilibrium concentration, and V is the volume of the water to be treated (e.g., 1000 L).

The simulated results of the above example are shown in Figure 2.10 from which one can estimate the mass of carbon required for a given fractional removal. As expected the mass of carbon increases exponentially for higher removal efficiencies. Similar plots may easily be constructed using Langmuir's parameters for various initial concentrations and fractional removal.

3 CONCLUSIONS

p-cresol is one of the most malodorous pollutants emitted from swine farming operations. Adsorption is one of the favorable technologies to mitigate *p*-cresol effectively. In this work, adsorption of *p*-cresol was studied using basic activated carbon. Optimum adsorption was found to be 12.02 mg g^{-1} at 25° C , pH of 7 and adsorbent dose of 3.2 g L^{-1} . Effect of temperature and pH was found to be not significant and a maximum theoretical adsorption capacity of 68 mg g^{-1} was obtained at temperature 25° C , neutral pH and adsorbent dose of 20 g L^{-1} . Analysis of the data suggested that adsorption was of second-order and predominantly of chemisorption type. In addition, overall adsorption was limited by external and internal mass transfer limitations and adsorption probably proceeded via electron transfer between activated carbon and phenol molecules.

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CHAPTER THREE

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

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This chapter “Adsorbents from pine wood via K_2CO_3 -assisted low temperature carbonization for adsorption of *p*-cresol” is submitted to Industrial Crops and Products.

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.

Keywords: Adsorption; *p*-cresol; pine wood; Kinetics; Isotherms; RSM

3.1 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-methylbutyraldehyde), 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 from atmospheric ozone affecting plant, animal, and human health (Schiffman et al., 2001). 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 best 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, 2012), wood particleboard wastes (Girods et al., 2009), corn (Park et al., 2010), dates stones (Alhamed, 2010), avocado kernel seeds (Rodrigues et al., 2011), tobacco residues (kilic et al., 2011), and 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;Mohan et al., 2012;Calvete et al., 2010;Calvete et al., 2009;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 ($> 500\text{ }^{\circ}\text{C}$) for manufacture of the adsorbent thus making the entire processes uneconomical for commercial-scale production. If adsorption were to be 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 ($265\text{-}435\text{ }^{\circ}\text{C}$) 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 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.

3.2 Experimental Method

3.2.1 Preparation of activated carbon

Wood chips of Loblolly pine (*Pinus taeda*), grown in North Carolina 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 hours as described by Ahmad and Alrozi, (2010). Various impregnation ratios (K_2CO_3 /Wood) were tested to determine the effect of K_2CO_3 loading on yield and performance of activated carbon. After impregnation for 8 hours, pine wood was washed thoroughly for 45 min. Subsequently these samples were dried at 70 °C for 12 hours. Activation of these dried K_2CO_3 impregnated samples was carried out at temperature (300-400 °C) with a hold time of (1.5-2.5 h) under nitrogen flow (2 L) at heating rate of 10 °C.min⁻¹.

3.2.2 Experimental Design

A central composite design (CCD) consisting of 2³ 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 3.1

Table 3.1 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
Held Time (h)	X ₂	1.59	1.5	2	2.5	2.84
IR	X ₃	0.32	1	2	3	3.68

3.2.3 Characterization of PAC

Specific surface areas of PAC and the original pine wood were determined by Brunauer–Emmett–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 (8h) of 0.4 g of activated char and 20 ml of de-ionized water (Sayed and Bandsoz, 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, Na₂CO₃ and NaHCO₃ (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.

3.2.4 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 x 0.25 mm x 0.25µm). Data was acquired using an oven temperature of 65 °C to 95 °C @ 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.

3.2.5 Adsorption Kinetics And Isotherms

To understand efficacy and mechanism of the *p*-cresol adsorption processes, data were analyzed using pseudo-first order (equation 1), pseudo-second order (equation 2), Elovich (equation 3) and intra-particle diffusion models (equation 4). Selection of the order

of reaction was based on the value of coefficient of determination (R^2) as described by (Kilic et al., 2011; Demribas et al., 2004; Aravindhnan et al., 2009; Allen et al., 2005).

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

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

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

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

In equations 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 ($\text{mg g}^{-1} \text{min}^{-1}$) 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 ($\text{mg g}^{-1} \text{min}^{-1}$) 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, 19160 (equation 5) and (Freundlich, 1906) (equation 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.

3.2.6 Effect of 2-methylbutrylaldehyde

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 in presence of 2-methylbutrylaldehyde (2-MB). Equal concentrations (500 mg L^{-1}) of *p*-cresol and 2-MB were mixed on a hot plate at 100 rpm and 25°C . The adsorption capacity of PAC was determined as explained previously and the data were analyzed using two-sample t-test.

3.2.7 Role of surface and dissolved oxygen

Oxygen is present in an adsorbed state on the PAC surface and dissolved state in the water. Based on previous research, it is expected that oxygen plays a significant role in phenol adsorption process (Terzyk, 2003; Valdes et al., 2002). Hence separate experiments were performed to reconfirm the effect of surface and dissolved oxygen on adsorption of *p*-cresol on PAC.

In the first phase, the surface oxygen content was enhanced via liquid phase oxidation and a gas phase oxidation as well. Liquid phase oxidation involved treating of PAC with conc. H₂SO₄ for 30 min followed by 40 min washing with DI water to remove traces of any acid. Gas phase oxidation was performed by treating the PAC with 18 g m⁻³ ozone for 30 min in a bed glass reactor. The adsorption capacity of oxidized samples were determined and compared with untreated samples of PAC using a one-way analysis of variance.

To determine the effect of dissolved oxygen (DO) (in water) we compared the adsorption capacity of PAC in normal DI water (DO \approx 7.8 mg L⁻¹) with oxygen-free DI water (DO \approx 0.0 mg L⁻¹) using a two-sample t-test. Oxygen free water was prepared by purging DI water continuously with ultra-high pure nitrogen until DO in the water decreased to near zero levels.

3.3 Results and Discussion

3.3.1 Development of model equation

Data collected from the central composite design was used to develop a polynomial model to describe the dependence of adsorption and PAC yield on carbonization temperature, carbonization time, and IR using JMP 9.0 (Cary, NC, USA) and Design-Expert 7.0 (Minneapolis, MN, USA). Adsorption was found to be in the range of 3.90 to 8.83 mg g⁻¹ where as char yield was in the range of 28.11 to 63.22%. Quadratic regression models were suggested for adsorption of *p*-cresol and char yield as below:

$$\hat{Y} = 71.9707 - 0.2310 X_1 - 22.9637X_2 - 6.1047X_3 + .0002x_1^2 + 2.8920x_2^2 + 0.0651x_3^2 + 0.0259x_1x_2 + 0.0082x_1x_3 + 1.6625x_2x_3 \quad (7)$$

$$\begin{aligned} \hat{Y} = & 410.9739 - 1.84473 X_1 - 10.5403X_2 - 21.9914X_3 + 0.0024x_1^2 + 1.5377x_2^2 \\ & - 5.7018x_3^2 - 0.0099x_1x_2 + 0.0004x_1x_3 \\ & - 0.07002x_2x_3 \end{aligned} \quad (8)$$

where X_1 , X_2 , and X_3 are carbonization temperature, carbonization time, and IR, respectively. The coefficients with one factor (X_1 , X_2 , X_3) represent the effect of one factor, while the coefficients with two factors (X_1X_2 , X_1X_3 , X_2X_3) and those with

second-order terms (X_1^2 , X_2^2 , X_3^2) represent the interaction between the two factors and quadratic effect respectively.

3.3.2 Effect of experimental conditions

Among all treatments tested, only temperature was found to have a significant effect on PAC yield ($p=0.0001$) (Fig. 3.1 A). However, adsorption capacity was not affected by carbonization temperature, carbonization time and IR ($p=0.3728$) (Fig. 3.1 B).

In addition, experimental conditions employed in this research were optimized using JMP 9.0 (Cary, NC) and Design-Expert 7.0 (Minneapolis, MN). However a single solution could not be achieved for adsorption and char yield as the solution was a saddle point, perhaps due to conservative ranges of the independent parameters (temperature, time and IR). The lack of single solution led to the selection of a condition based on maximum char yield. Optimized parameters selected were carbonization temperature of 266 ° C, carbonization time of 2 h, and IR of 2 that provided an experimental char yield of 63.22 % and adsorption of 5.40 mg g⁻¹.

1.

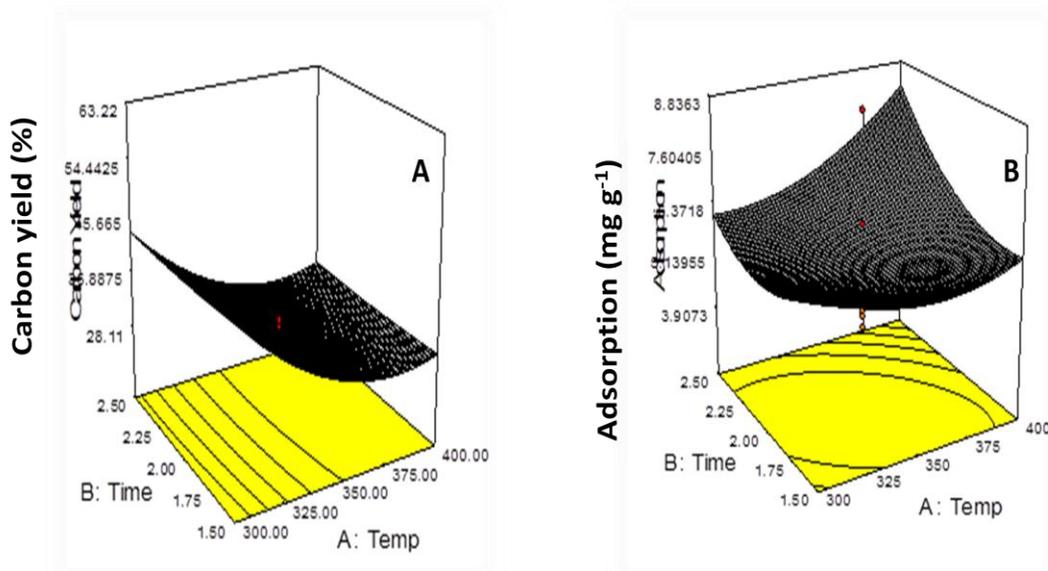


Figure. 3.1. Effect of carbonization time and temperature on yield of PAC (A) and adsorption of *p*-cresol on PAC (B).

3.3.3 Characterization of PAC

Several researchers including (Foo and Hameed, 2012a; Foo and Hameed, 2012b) described that under inert condition, K_2CO_3 is dissociated to K, K_2O , CO and CO_2 via different reactions. These potassium compounds formed during the activation step would diffuse into the internal pore structure of char there by widening existing pores and creating more new pores to facilitate adsorption. However, in this study the BET surface area of PAC did not change substantially as a result of carbonization ($22.54 \text{ m}^2\text{g}^{-1}$ versus $21.23 \text{ m}^2\text{g}^{-1}$), perhaps due to use of lower temperature. But, comparison of SEM micrographs of uncarbonized pine wood (control) (Fig. 2A) and PAC (Fig. 2B) revealed alteration of the

physical structure. In addition, PAC exhibited significant adsorption capacity ($p=0.00006$) when compared to control perhaps due to the change in the surface chemistry (Moreno-Castilla, 2004). Specifically, when we determined the acid value of the surface, it was found that carbonization (with K_2CO_3) increased the acid value from 5.01 to 9.29 thereby making the surface more basic than original pinewood (control sample). The enhancement in surface basicity was also confirmed via Boehm titration which suggested that concentration of basic functional groups on surface increased significantly due to reaction between K_2CO_3 with carbon during carbonization (Table 3.2).

Table 3.2. Characterization of surface chemistry of the PAC.

Sample	BET Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Acidic groups (mmol g ⁻¹)				Basic group (mmol g ⁻¹)	PZC	Acid value
			Carboxylic	Lactonic	Phenolic	Total			
Pine wood	22.54	0.0091	0.16	0.17	0.25	0.58	0.05	5.83	5.01
PAC	21.23	0.0021	0.25	0.25	0.50	1.00	1.58	8.78	9.29

Adsorption capacity of carboneous material in its molecular form depends on the electron density of the adsorbate. *p*-cresol exhibits electron donating mechanism with the basic surface of the adsorbate, due its electron donating methyl and hydroxyl groups. This mechanism becomes the driving force for increase in adsorption (Singh et al., 2008). Another reason for increase in adsorption may be due to formation of covalent bonding on the surface of carbon, as a result of reaction between phenoxy radicals and the active sites of the carbon surface (Terzyk, 2003). Considering the experimental results, it is clear that π - π interaction is the dominating mechanism for adsorption.

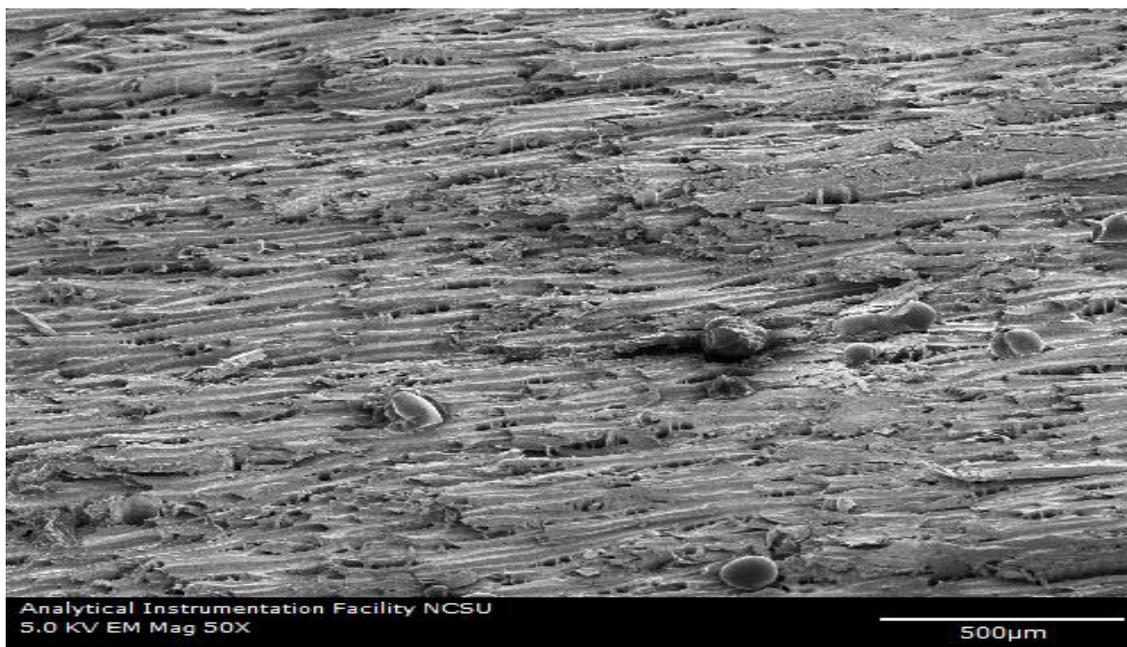


Figure 3.2 A: pine wood

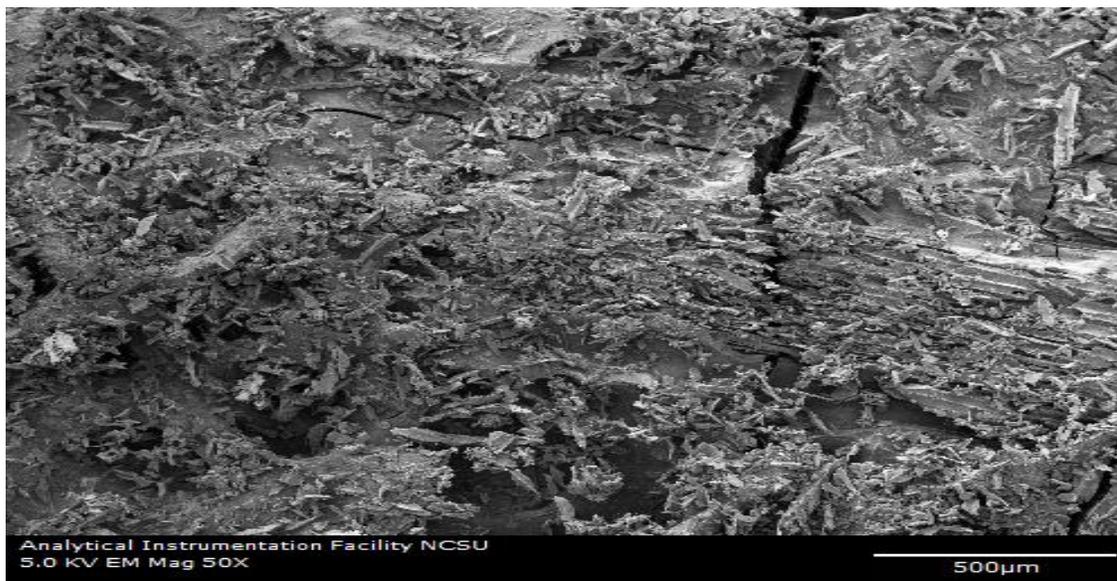


Figure 3.2 B: Optimized

3.3.4 Adsorption isotherm and thermodynamics

Adsorption isotherm for temperatures 15-55 ° C are shown in Fig. 3.3A. When data was analyzed using linearized Freundlich and Langmuir isotherm models (Fig. 3.3B, Fig. 3.3C and Table 3.3) the data conformed to the Langmuir model ($R^2 = 0.99$) suggesting monolayer adsorption. In our research, a theoretical maximum adsorption capacity 6.97 mg g⁻¹ was obtained at 25 ° C which was somewhat lower than values reported by Singh et al. (2008) and other researchers. For example, 2,4-dichlorophenol was studied using maize cob-based activated carbon by Satishkumar et al. (2009). The authors reported a maximum

adsorption capacity of about 17.9 mg g^{-1} . Kilic et al. (2011) reported phenol adsorption capacities of 17.83 and 0.55 mg g^{-1} for activated carbons synthesized from tobacco stalks using K_2CO_3 and KOH respectively. Singh et al. (2008) reported a maximum adsorption capacity of 63 mg g^{-1} for *p*-cresol on tested activated carbon from carrot weed (parthenium). Similarly, activated carbon from avocado kernel seeds was tested as an adsorbent for removal of phenol by Rodrigues et al. (2011) who reported an adsorption capacity of $87\text{-}90 \text{ mg g}^{-1}$. The lower adsorption capacity may be attributed to lower carbonization temperatures (265°C) employed in our research. According to Zhou et al. (2010), lower temperature leads to higher proportion of acidic groups such as carboxylic and lactonic groups which might decrease adsorption. However, it may be noted that considering that lagoon water generally contains less than 1 mg L^{-1} of *p*-cresol, the adsorption obtained in this research may be considered to be adequate.

Adsorption rate is dependent on temperature as it alters the molecular interactions and the solubility. The enthalpy of adsorption ΔH is related to the Langmuir constant b . The modified Gibbs free energy can be written as (Singh et al., 2006).

$$\ln b = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where b , ΔG° , ΔH° , ΔS° , R and T are the Langmuir constant, Gibbs free energy, enthalpy change, entropy change, gas constant and temperature respectively. In our research, a negative value ($-2.11 \text{ kJ mol}^{-1}$) of ΔH° indicates that the adsorption process is exothermic which was also supported by the decreased adsorption capacity at higher temperature. So, at

higher temperature the bond between *p*-cresol and the char surface is probably disrupted leading to desorption-dominant regime. Similar results were reported by Mohan et al. (2011) who observed that adsorption of fluoride by pine wood char decreased from 6.34 mg g⁻¹ at 35 °C to 4.46 mg g⁻¹ at 45 °C.

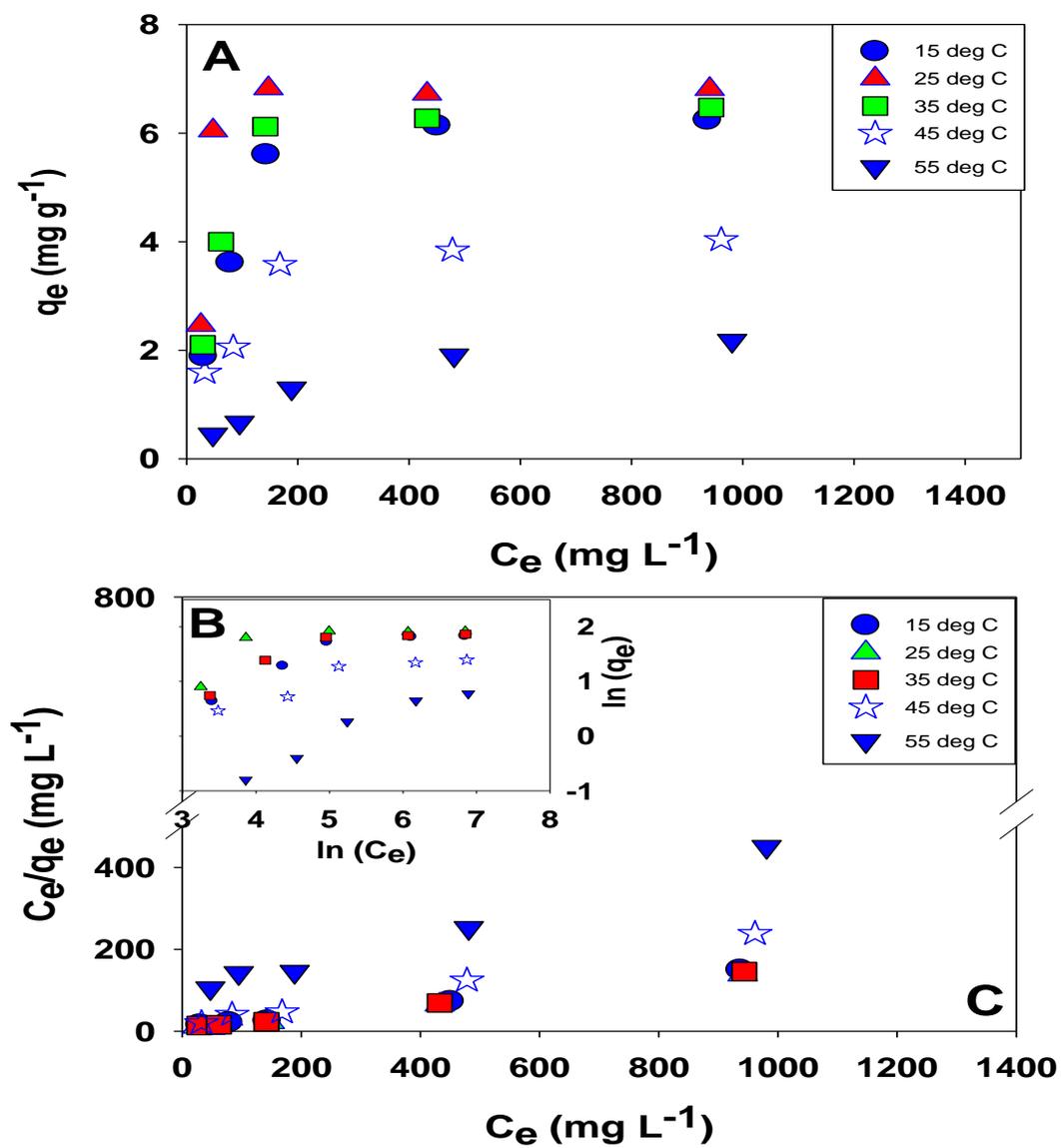


Figure 3

Figure. 3.3. Adsorption isotherms of *p*-cresol on PAC (A) using linearized Freundlich (B) and Langmuir models (C).

Table 3.3 Adsorption isotherm constants for *p*-cresol adsorption onto PAC.

Temp (°C)	Langmuir			Freundlich		
	Q ₀	b	R ²	K _F	n	R ²
15	6.68	0.018	0.99	0.60	3.00	0.79
25	6.97	0.051	0.99	0.21	4.67	0.51
35	6.79	0.024	0.99	1.50	3.39	0.75
45	4.30	0.016	0.99	0.33	3.45	0.86
55	2.76	0.004	0.99	0.45	1.84	0.94

3.3.5 Kinetics and mass transfer

The pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion model parameters were fitted to the data collected over the temperature range of 15-55 ° C. On a relative basis, Elovich ($R^2 = 0.82$), and intra-particle diffusion ($R^2 = 0.89$) models described the adsorption process better than pseudo-first order ($R^2 = 0.45$) and pseudo-second order ($R^2 = 0.67$) model (Table 3.4). Model parameters fitted better to the Elovich model indicated that adsorption to proceed via chemisorption (Tseng et al., 2003). Fig. 4 shows the plot of intra-particle diffusion model in which shape of curves seems be combination of two linear equations, suggesting involvement of two mechanisms. The first portion may be explained as gradual adsorption where intra-particle diffusion is the rate limiting step where

as the second portion can be described as equilibrium stage where intra-particle diffusion slows down due to attainment of equilibrium. A similar result was reported by Rodrigous et al. (2011) for removal of phenol by avocado kernel seeds, where it was found that intra-particle diffusion to be the rate-limiting factor. In addition, in the intra-particle diffusion equation, the value of constant C is not zero which indicates that intra-particle is not the rate limiting and other kinetic processes are also contributing to the mechanism.

To support the type of adsorption phenomenon associated with this study additional desorption experiments were performed with spent PAC using water as desorbing agent. Experiments were carried out similar to the batch adsorption experiments for 2 hours at 25 °C and it appeared that there was no desorption at all, suggesting chemisorption as the dominant form of adsorption.

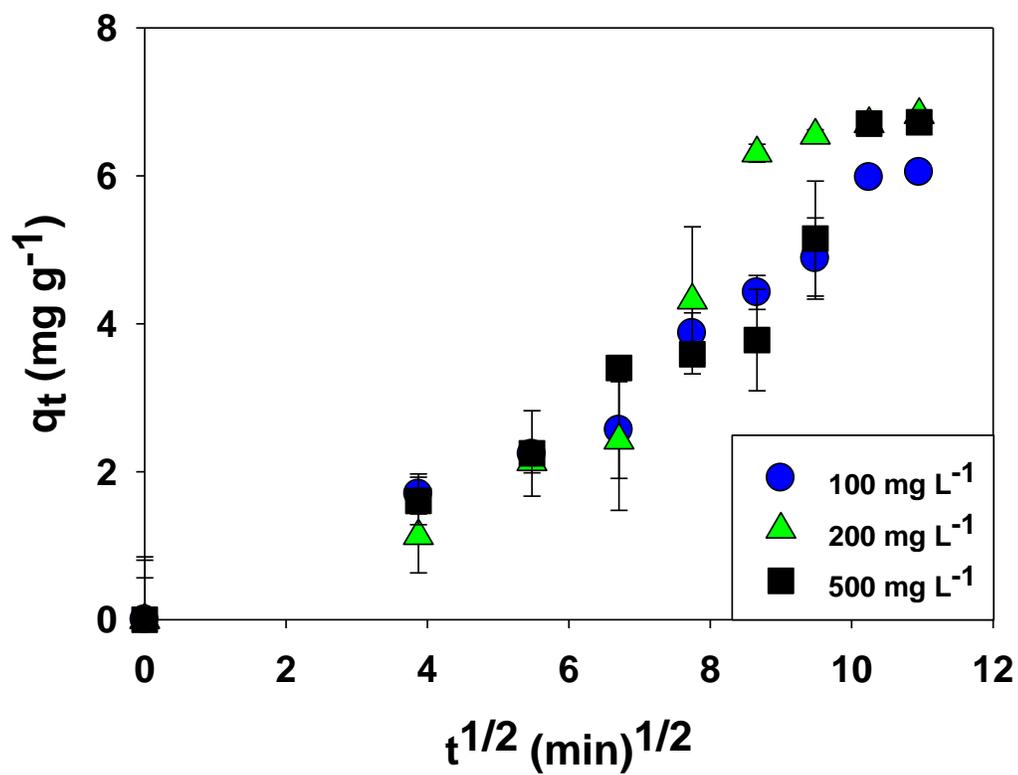


Figure 4

Figure 3.4: Intra-particle diffusion model for adsorption of *p*-cresol on PAC. Experimental conditions: Adsorbent dose: 10 g L^{-1} , 100 rpm, and unadjusted pH.

Table 3.4. Kinetic parameters for adsorption of *p*-cresol.

Experi men t (Temp_Co nc)	Pseudo 1 st order		Pseudo 2 nd order		Elovich		Intra-particle			
	R ²	K ₁	R ²	K ₂	R ²	α	β	R ²	K _p	c
15_50	0.523	0.038	0.960	0.027	0.960	0.479	2.396	0.967	0.180	0.106
15_100	0.289	0.161	0.650	0.001	0.970	0.830	1.238	0.883	0.331	0.533
15_200	0.815	0.017	0.650	0.004	0.800	1.633	0.927	0.895	0.496	0.053
15_500	0.307	0.023	0.987	0.015	0.972	1.390	0.726	0.904	0.571	0.837
15_1000	0.763	0.020	0.732	0.003	0.808	2.190	0.796	0.946	0.585	0.447
25_50	0.311	0.009	0.898	0.012	0.908	1.011	1.878	0.976	0.237	0.021
25_100	0.6	0.025	0.705	0.002	0.805	2.246	0.815	0.956	0.575	0.511
25_200	0.705	0.029	0.355	0.001	0.725	2.961	0.656	0.897	0.729	1.073
25_500	0.459	0.030	0.638	0.002	0.758	2.427	0.763	0.920	0.621	0.667
25_1000	0.697	0.019	0.790	0.005	0.838	1.691	0.797	0.916	0.564	0.059
35_50	0.010	0.001	0.994	0.143	0.950	0.535	2.128	0.786	0.184	0.513

Table 3.4 continued

35_100	0.545	0.023	0.790	0.011	0.843	1.594	1.218	0.948	0.374	0.163
35_200	0.827	0.018	0.778	0.003	0.832	1.983	0.852	0.961	0.542	0.305
35_500	0.448	0.033	0.678	0.002	0.803	2.408	0.774	0.953	0.650	0.606
35_1000	0.741	0.233	0.878	0.004	0.894	0.802	1.613	0.984	1.373	0.727
45_50	0.087	0.008	0.932	0.058	0.904	0.016	3.072	0.817	0.133	0.275
45_100	0.126	0.009	0.939	0.023	0.929	0.560	2.184	0.916	0.196	0.134
45_200	0.784	0.012	0.538	0.002	0.780	2.073	1.175	0.923	0.393	0.395
45_500	0.385	0.006	0.484	0.002	0.735	2.132	1.265	0.915	0.379	0.510
45_1000	0.778	0.016	0.070	0.003	0.788	2.175	1.213	0.938	0.387	0.470
55_50	0.045	0.004	0.234	0.131	0.612	0.013	11.41	0.784	0.042	0.063
55_100	0.001	0.006	0.354	0.126	0.514	0.787	8.045	0.514	0.535	0.038
55_200	0.039	0.005	0.910	0.034	0.880	0.303	3.305	0.888	0.130	0.454
55_500	0.542	0.011	0.660	0.009	0.796	0.998	2.754	0.933	0.169	0.138
55_1000	0.463	0.309	0.299	0.003	0.618	1.594	2.232	0.774	0.216	0.300

3.3.6 Effect of 2-methylbutrylaldehyde

Effect of mixtures on competitive effect of *p*-cresol in presence of 2-MB was studied in batch experiments at 25 °C, unadjusted pH, 500 mg L⁻¹ concentration and adsorption dose of 10 g L⁻¹. It was found that there was no significant difference ($p=0.97$) (Fig. 3.5A and B) in adsorption suggesting that 2-MB molecules were not competing with *p*-cresol for the same active site during adsorption. This is favorable considering that in actual swine lagoons contain many organic compounds and their presence does not hinder adsorption of *p*-cresol.

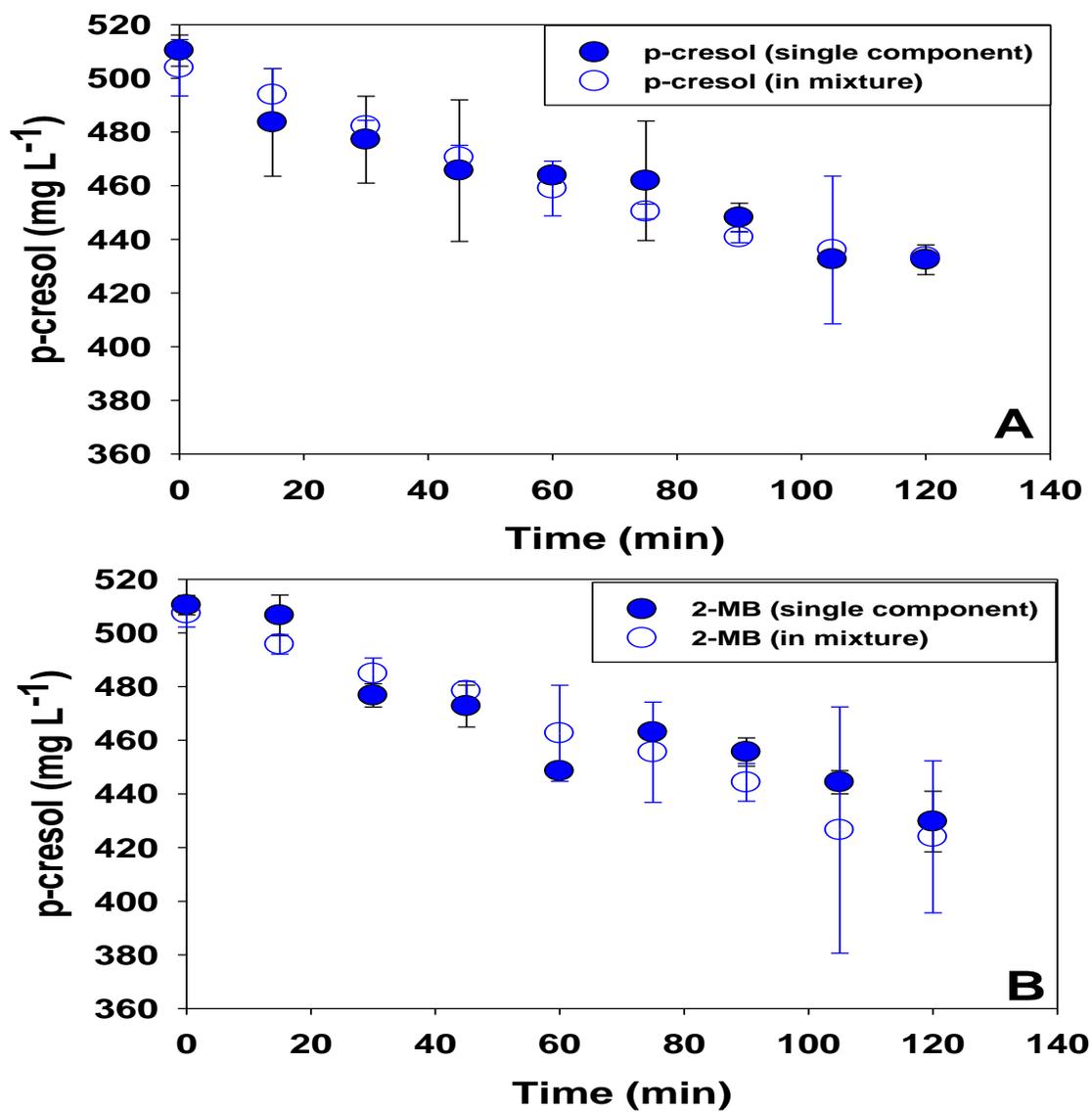


Figure. 3.5. Adsorption of *p*-cresol on PAC in presence of 2-MB (A) and adsorption of 2-MB in presence of *p*-cresol (B).

3.3.7 Role of surface and dissolved oxygen

As expected, surface oxygen has a significant negative impact on adsorption of *p*-cresol ($p=0.05$). But, the performance of ozone-treated PAC and sulfuric acid-treated char during were significantly different ($p=0.0002$) (Fig. 3.6A). Although both oxidative treatments enhanced surface oxygen, ozone treated char exhibited significantly lesser adsorption capacity than sulfuric acid treated char. As suggested by Valdes et al. (2002), reaction of char with ozone may have significantly enhanced carboxylic groups on the surface that may have decreased the adsorption capacity. Due to increase in competition with water, along with weakening of forces between the π band of the carbon planes and π electron system of the aromatic rings, adsorption of *p*-cresol on ozonated PAC was decreased (Radovic et al., 2000). Treatment with sulfuric acid also impacted adsorption due to formation of sulfonic, carboxylic, lactone and phenolic groups. The adsorption capacity of ozone treated char was less than that of H_2SO_4 -treated char because of increase in carboxylic and ether groups that changed the polarity of the carbon surface (Park and Jin, 2005). Sulfuric acid treated char is highly acidic as it is susceptible to provide two protons, presence of sulfonic and lactone groups make it a good adsorbent when compared with ozone (Li et al., 2011). Another reason for ozone-treated PAC to exhibit lower adsorption capacity than H_2SO_4 treated PAC may be due to increase in hydrophilicity.

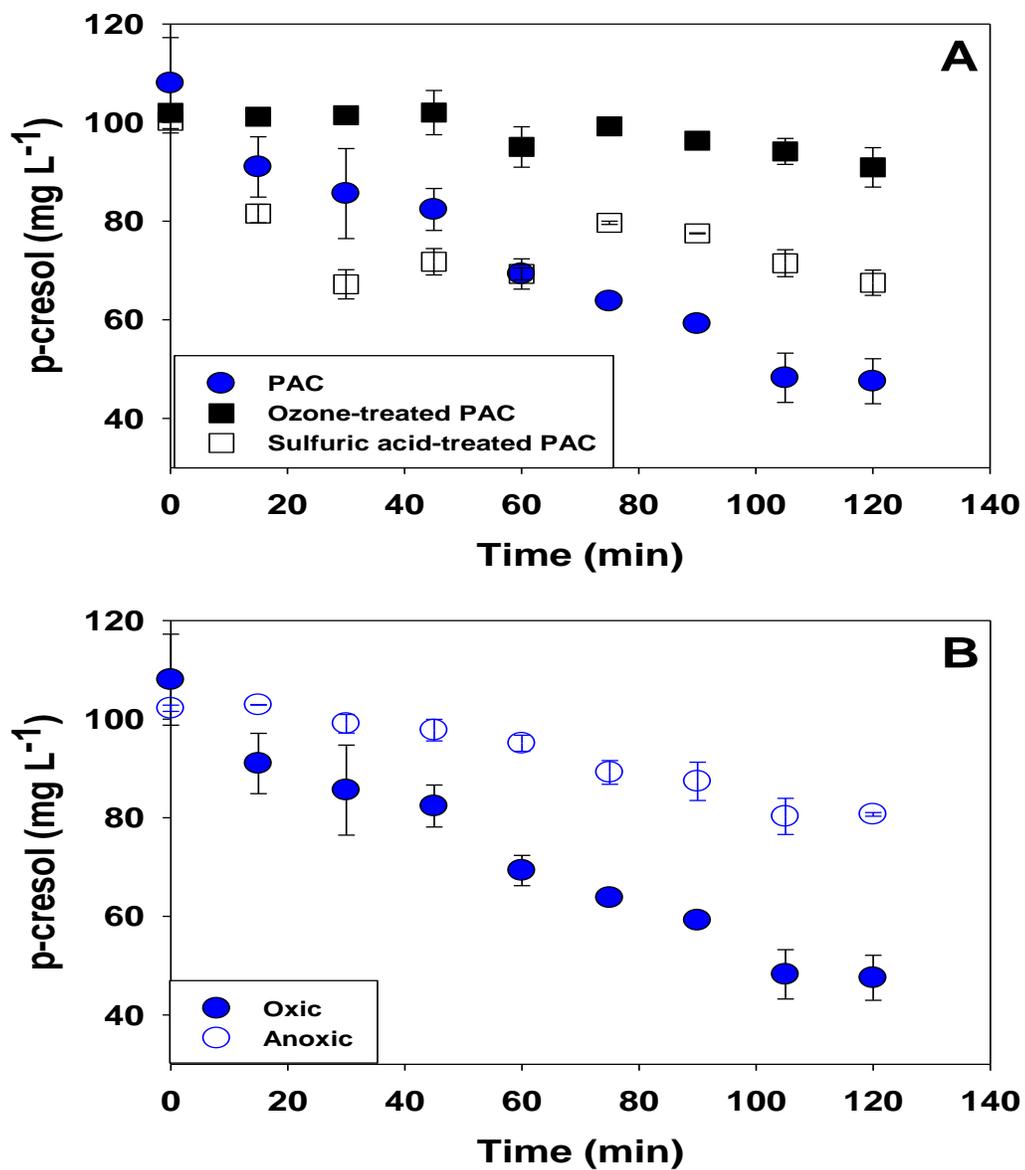


Figure 6

Figure. 3.6. Effect of nature of surface oxygen (A) and dissolved oxygen (B) on adsorption of *p*-cresol on PAC.

Additionally, anoxic condition in the solution also decreased the adsorption capacity of the activated char ($p=0.01$) (Fig. 3.6B). Similar findings were reported by Tessmer et al. (1997) and Radovic et al. (2000) who proposed that oxygen participated in oxidative coupling polymerization reactions that resulted in irreversible adsorption on the surface (Cooney and Xi, 1994) (Figure 3.7).

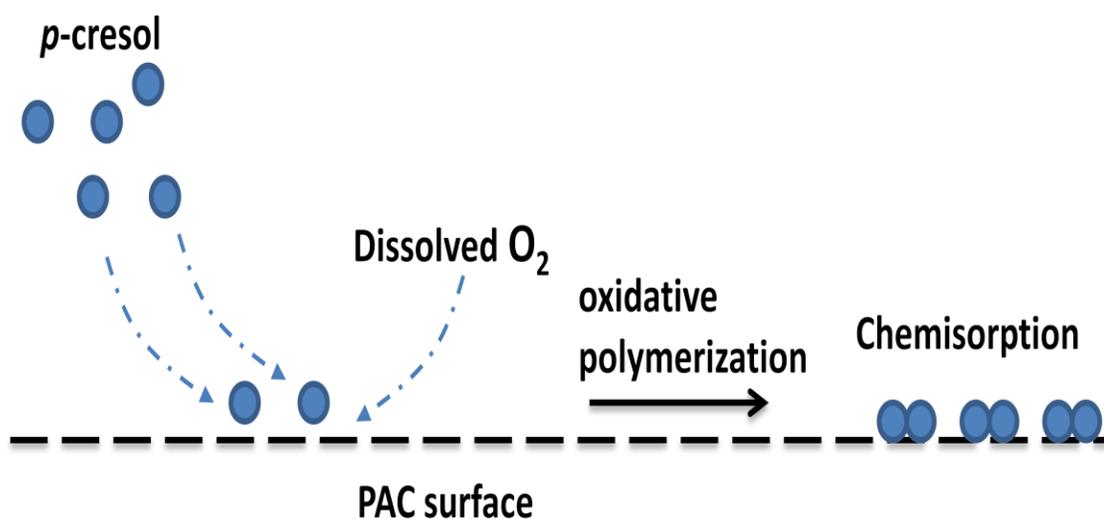


Figure. 3.7. Proposed mechanism of adsorption of *p*-cresol on PAC

3.4 CONCLUSIONS

PAC was found to be effective in adsorbing *p*-cresol. The kinetic studies indicated that adsorption of *p*-cresol molecules onto PAC followed Elovich and intra-particle diffusion model suggesting chemisorption as the predominant mechanism. Optimum char yield and adsorption was found to be 63.22 % and 5.40 mg g⁻¹ respectively. The equilibrium data agreed with Langmuir's model and maximum theoretical adsorption capacity of 6.97 mg g⁻¹ was obtained at temperature 25 °C, unadjusted pH and adsorbent dose of 10 g L⁻¹. In addition, it was found that adsorption decreased with an increase in temperature suggesting an exothermic process.

3.5 References

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CHAPTER FOUR

Summary and Conclusion

The goal of this research was to synthesize low-cost adsorbent for mitigation of *p*-cresol from swine farming operation. The objectives were to: (1) synthesize low-cost pine wood activated carbon (PAC) by optimizing carbonization time, impregnation ratio (IR), and carbonization temperature (2) characterize the PAC, (3) study adsorption kinetics and isotherms, (4) determine the effect of 2-methylbutyraldehyde on adsorption of *p*-cresol, and (5) confirm the role of dissolved and surface oxygen on adsorption of *p*-cresol.

The objectives for this study were accomplished in two phases. In the first phase, a commercial granular activated carbon (GAC) was used for studying the adsorption of *p*-cresol. The purpose of using GAC was to divulge the adsorption mechanism and to understand the role of functional groups present on the surface, which facilitates adsorption, eventually which will help in synthesizing an activated carbon from pine wood. The first phase started with a hypothesis that *p*-cresol would need a basic activated carbon. In this study, the main focus was to examine the combined effect of temperature, pH and adsorbent dose on adsorption and its optimization. At the same time, adsorption of *p*-cresol in presence of Isovaleric acid (IVA) and formaldehyde was tested and results indicated an increase in adsorption of *p*-cresol in presence of these compounds. The results indicated that adsorbent

dose has significant effect on adsorption where as temperature and pH were insignificant towards adsorption. Kinetic data suggested a second order reaction and adsorption of *p*-cresol proceeded via chemisorption as suggested by several researchers. Optimum adsorption was found to be 12.02 mg g^{-1} at $25 \text{ }^\circ\text{C}$, pH of 7 and adsorbent dose of 0.32 g and a maximum theoretical adsorption capacity of 68 mg g^{-1} were obtained at a temperature of $25 \text{ }^\circ\text{C}$, neutral pH and adsorbent dose of 20 g L^{-1} . Adsorption of *p*-cresol increased significantly when 1000 ppm each of IVA and formaldehyde were present in the mixture.

Information from the first phase was used to synthesize activated char from pinewood.

Preliminary experiments suggested that K_2CO_3 was a better activating agent than KOH and H_3PO_4 for preparation of basic activated char. A central composite design was used to study the effects of carbonization time, impregnation ratio (IR), and carbonization temperature on the yield and efficacy of pinewood char. Optimum carbon yield and adsorption was found to be 63.22 % and 5.40 mg g^{-1} respectively. Adsorption was found to be of chemisorption type and equilibrium data fitted well to Langmuir model with a maximum theoretical adsorption capacity of 6.97 mg g^{-1} at $25 \text{ }^\circ\text{C}$, unadjusted pH and adsorbent dose of 10 g L^{-1} . Although we did not see any significant change in surface area, we could see a significant increase in adsorption capacity as a result of K_2CO_3 assisted carbonization. Effect of surface oxygen and dissolved oxygen on adsorption was also tested which confirmed that presence of oxygen decreased the *p*-cresol uptake capacity. The decrease may be due to presence carboxylic and

lactones groups which reduced the adsorption capacity of the carbon. Effect of mixtures on competitive effect of *p*-cresol in presence of 2-methylbutyraldehyde was studied in batch experiments at 25 °C, unadjusted pH, 500 ppm concentration and adsorption dose of 10 g L⁻¹. The results indicated that there was no significant effect. Adsorption reaction was mainly due to formation of hydrogen-bonding between the hydroxyl groups of *p*-cresol and functional groups on the carbon surface.

Considering that fact that adsorption is one of the most preferred and practical methods for mitigation of organic pollutants there is a significant scope to use adsorption as an option for treating lagoon water. Hence future research is suggested in exploring new agricultural waste resources such as tobacco stalk for synthesis of adsorbents. Additionally, microwave-assisted carbonization could be explored to minimize the heating requirements needed for deconstruction/carbonization processes