

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 (CH₃)C₆H₄(OH), 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 the 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 the 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 fairly 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 using GAC could effectively mitigate *p*-cresol released from swine facilities.

Keywords: adsorption; *p*-cresol, activated carbon, kinetics; isotherms; RSM, USA

Citation: Das, L., P. Kolar, J. A. Osborne and J. J. Classen. 2012. Adsorption of *p*-cresol on granular activated carbon. Agric Eng Int: CIGR Journal, 14(4): 37–49.

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 (CH₃)C₆H₄(OH), 4-methylphenol). The concentration *p*-cresol in swine facilities vary widely between 4 µg L⁻¹ and 2 mg L⁻¹ depending on the age and storage conditions of the manure (Yao et al., 2011; Wu et al., 1999). Wu et al.

(1999) observed up to 167 mg L⁻¹ of *p*-cresol in manure samples that were stored for three weeks. However, toxicity and adverse effects of *p*-cresols on human skin, eyes, respiratory track, mood and mental health can be felt even at very low concentrations due to which the United States Environmental Protection Agency categorized *p*-cresol as priority pollutant (Schiffman et al., 1995; Singh et al., 2008; 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

Received date: 2012-06-13 Accepted date: 2012-09-04

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process in which certain surfaces attract specific compounds (pollutants) due to the physical and chemical interactions between the surface and the pollutants (Dabrowski, 2001). Due to large surface area, porous structure, and favorable chemistry, activated carbon and other similar materials have 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 research works on adsorption of *p*-cresol on activated carbons. Singh et al. (2008) reported adsorption of *p*-cresol using a parthenium-based activated carbon. This research also suggested that 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 the 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 their 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 effects 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 method

2.1 Materials

Commercial granular activated carbon (GAC) derived

from coconut shell (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 employed to determine the effects of temperature, pH and adsorbent dose. 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 six 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 augmented this design with more extreme levels (denoted as α in Table 1).

Table 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 /°C	X_1	8.18	15	25	35	41.82
Adsorbent dose/g L ⁻¹	X_2	30	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, enabled estimation of nonlinear dependencies of adsorption on adsorption dose, pH, and temperature. The levels of the axial points, coded as $+\alpha$ and $\alpha=1.682$, were chosen so that design was rotatable. This meant 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 eight factorial points, six axial points and six 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 (X_1), adsorbent dose (X_2), and pH (X_3) using a second degree polynomial (Equation (1)) 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 using 100 mg L⁻¹ of *p*-cresol solution whose pH was adjusted using 0.1N H₂SO₄ and diluted NaOH. Typically, 100 mL of *p*-cresol solution was mixed with 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 r min⁻¹ 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 × 0.25 mm × 0.25 μm). Data was acquired using an oven temperature of 105°C to 185°C at 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 2):

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

where, q_t (mg g⁻¹) is the adsorption capacity; c_0 and c_t (mg L⁻¹) are liquid-phase concentrations of *p*-cresol at the beginning of the experiment ($t = 0$) and at any time ($t = t$), 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 were expected to be found in swine lagoons. A mixture of *p*-cresol (1,000 mg L⁻¹), IVA (1,000 mg L⁻¹), and formaldehyde (1,000 mg L⁻¹) (with traces of methanol) in DI water was prepared and mixed with 20 g L⁻¹ 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 and 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) to (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 (mg g⁻¹ min⁻¹) are the first and second order rate constants which are obtained from the plots of $\log(q_e - q_t)$ vs t and t/q_t vs t . For Elovich model, α (mg g⁻¹ min⁻¹) and β (g mg⁻¹) are the initial adsorption rate and desorption constants. k_p is intra-particle diffusion rate 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 is 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 r m^{-1} 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 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 20 g L^{-1} 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 H_2SO_4 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. Two grams 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 was described by Love et al. (2011).

3 Results and discussion

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 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 model for adsorption of *p*-cresol in terms of coded value is given in Equation (9).

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

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 effects respectively. The positive sign indicates synergistic effect, while negative sign indicates antagonistic effects (Ahmad et al., 2009).

Analysis of data indicated that neither temperature ($15\text{-}25^\circ\text{C}$) nor pH (6-8) had any effects 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.

Table 2 Central composite experimental design matrix

Run	X_1 : Temp. code	X_2 : Adsorbent dose code	X_3 : pH code	Temperature /°C	Adsorbent dose /g L ⁻¹	pH	Adsorption (actual) /mg g ⁻¹	Adsorption Predicted /mg g ⁻¹
1	-1	-1	-1	15	10	6	6.40 ± 0.37	6.97
2	1	-1	-1	35	10	6	7.28 ± 0.47	7.88
3	-1	1	-1	15	30	6	3.06 ± 1.41	3.18
4	1	1	-1	35	30	6	3.09 ± 0.59	2.77
5	-1	-1	1	15	10	8	6.48 ± 0.87	7.23
6	1	-1	1	35	10	8	8.00 ± 0.78	8.32
7	-1	1	1	15	30	8	3.24 ± 1.09	3.09
8	1	1	1	35	30	8	2.98 ± 0.62	2.86
9	-1.682	0	0	8.182	20	7	4.48 ± 0.84	3.92
10	1.682	0	0	41.818	20	7	4.57 ± 0.32	4.50
11	0	-1.682	0	25	31.80	7	12.02 ± 0.43	10.90
12	0	1.682	0	25	36.82	7	2.64 ± 0.90	3.13
13	0	0	-1.682	25	20	5.318	4.78 ± 0.69	4.42
14	0	0	1.682	25	20	8.681	4.98 ± 0.22	4.71
15	0	0	0	25	20	7	4.52 ± 0.40	4.87
16	0	0	0	25	20	7	4.76 ± 0.19	4.87
17	0	0	0	25	20	7	5.12 ± 0.28	4.87
18	0	0	0	25	20	7	4.95 ± 0.30	4.87
19	0	0	0	25	20	7	4.62 ± 0.25	4.87
20	0	0	0	25	20	7	5.11 ± 0.16	4.87

3.2 Effect of temperature

Figure 1a and b show the interactive effects 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 were different than those reported by Ravi et al. (1998) who found that adsorption increased with the 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 the 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 Effects 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. Combined effects of pH with temperature and adsorbent doses are illustrated in Figure 1a and c respectively. The effects on adsorption due to pH and adsorption dose

is shown in Figure 1b, 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 effects of adsorption dose and temperature, adsorption dose and pH are shown in Figure 1b and c respectively. It is evident that temperature and pH are not playing any roles in adsorption in comparison with the adsorption dose ($p = 0.0001$). Adsorption increases with the decrease in adsorbent dose; this observation can be understood as the increase in number of adsorption sites with the 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 the decrease in adsorbent dose. These findings are in good agreement with results reported by Huang (2009) and Helen et al. (2009).

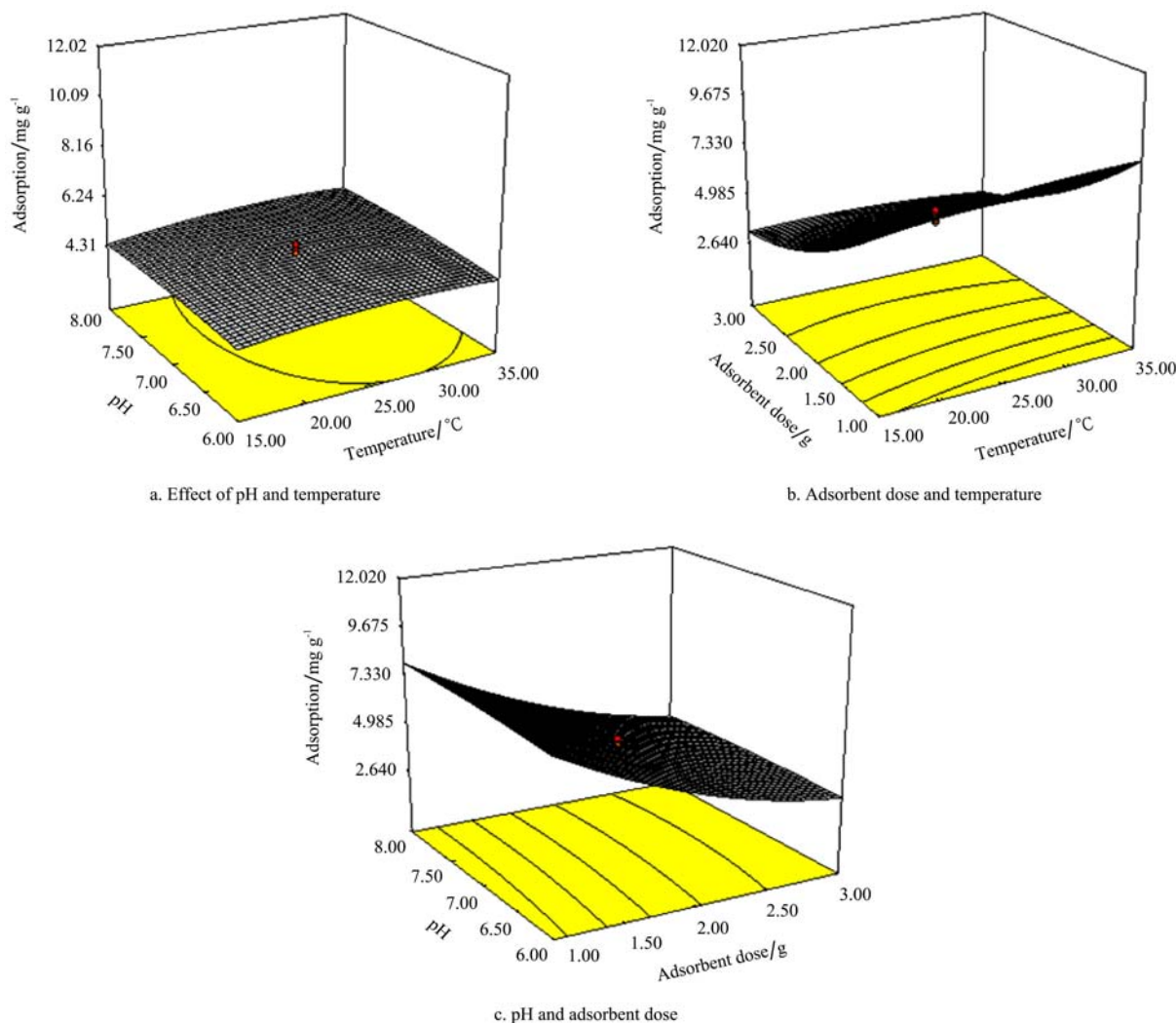


Figure 1 Surface plots of adsorption of *p*-cresol to describe combined effects

3.5 Optimization of *p*-cresol adsorption

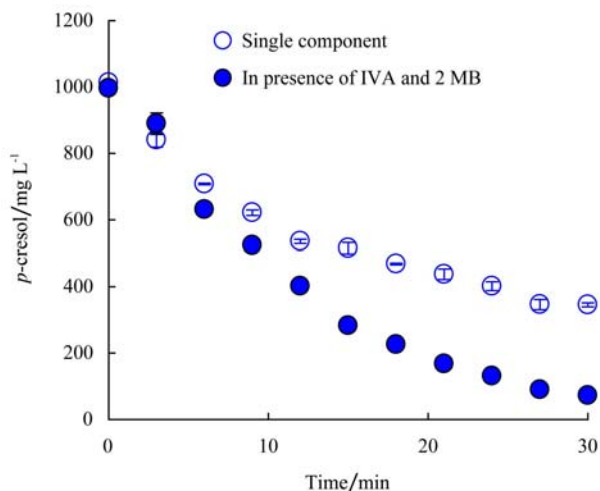
The experimental conditions used to obtain data were optimized using JMP 9.0 (SAS, Cary, NC) and Design-Expert 7.0 (Minneapolis, MN). However, a single solution could not be achieved as the solution was a saddle point, perhaps due to conservative ranges of the independent parameters (temperature, adsorbent 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 the

temperature of 25°C, the pH of 7 and the adsorbent dose of 3.2 g L⁻¹. As temperature and pH had no effects 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 was close to the optimized value (Table 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 1,000 mg L⁻¹ each of IVA and formaldehyde were present in the mixture (Figure 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.



Note: Experimental conditions: IVA , formaldehyde, and *p*-cresol = 1,000 mg L⁻¹ each, Temperature = 25°C

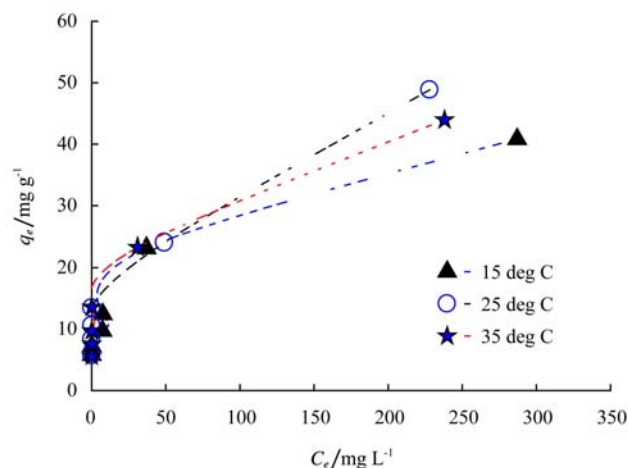
Figure 2 Effect of IVA and formaldehyde on adsorption of *p*-cresol on activated carbon (*n*=2)

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 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 the 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 m² g⁻¹ respectively. Similarly Ayranci and Duman (2005) observed maximum adsorption capacity of 207.64 mg g⁻¹ and a surface area of 1464 m² g⁻¹, whereas Huang (2009) recorded maximum adsorption capacity 248.1 mg g⁻¹ with a surface area of 727 m² g⁻¹. In this study surface area was 662 m² g⁻¹ but maximum adsorption capacity was 68 mg g⁻¹ clearly suggesting that surface area and porosity did not influence the uptake of *p*-cresol as was also observed by Daifullah and Gigris (1998).



Note: Experimental conditions: pH: 5.8 and adsorbent dose: 20 g L⁻¹

Figure 3 Adsorption isotherms of *p*-cresol at 15, 25, and 35°C

Table 3 Adsorption isotherm constants for *p*-cresol adsorption onto GAC

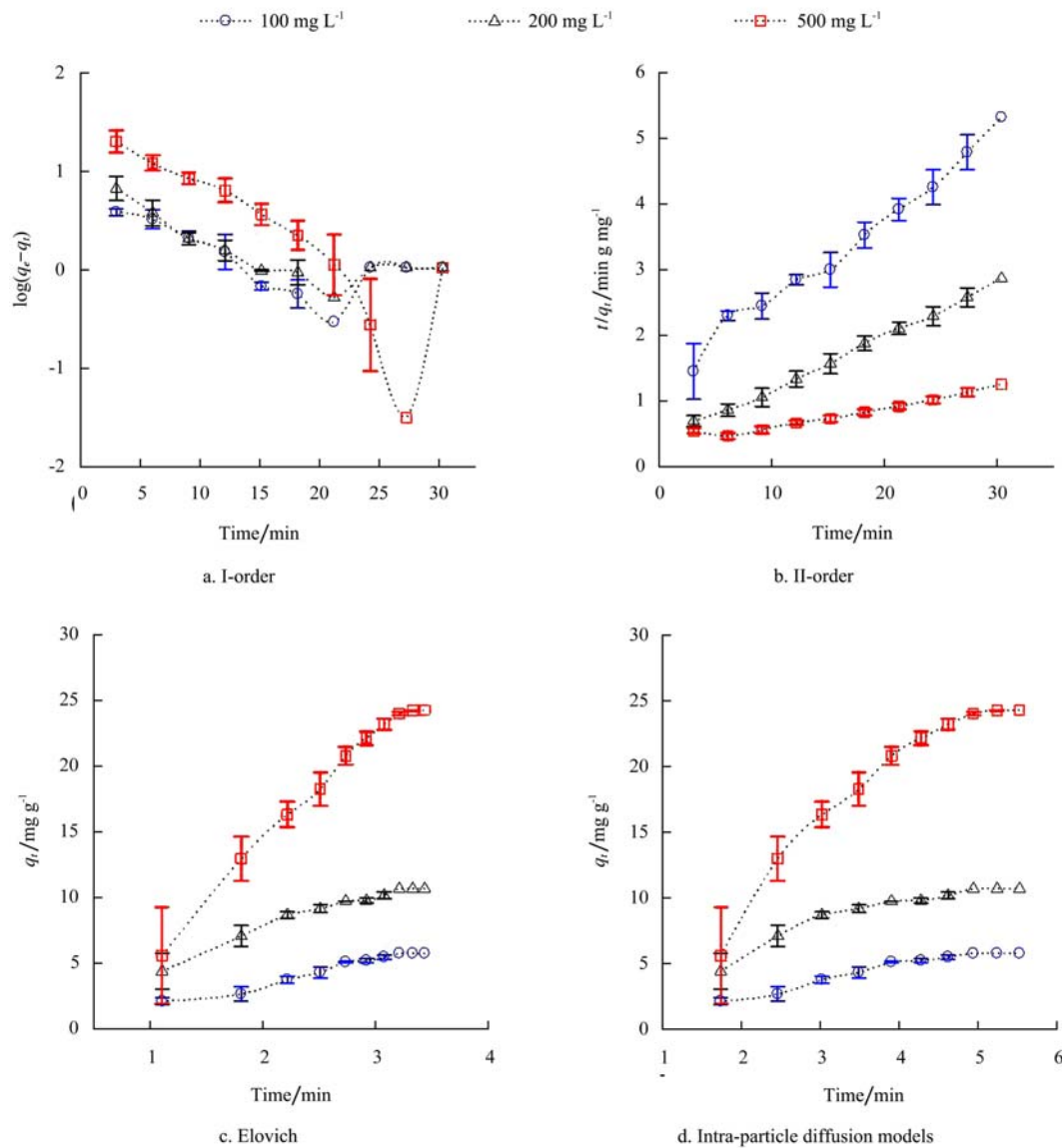
Temp /°C	Langmuir			Freundlich		
	Q_0 /mg g ⁻¹	B /L mg ⁻¹	R^2	K_F / (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	1/n	R^2
15	43.7	0.038	0.89	6.25	0.33	0.89
25	68	0.01	0.69	3.99	0.46	0.7
35	52	0.02	0.65	8.0	0.31	0.65

3.8 Kinetics and mass transfer

Pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion model parameters were calculated using Equations (3), Equation (4), Equation (5), and Equation (6) respectively. Figure 4a-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 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).



Note: Experimental conditions: Temperature: 25°C, pH: 5.8, and adsorbent: 20 g L⁻¹.

Figure 4 Representative kinetic plots

Table 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	$k_2 / \text{mg g}^{-1} \text{min}^{-1}$	R^2	$\alpha / \text{mg g}^{-1} \text{min}^{-1}$	$\beta / \text{g mg}^{-1}$	R^2	$k_p / \text{mg g}^{-1} \text{min}^{-0.5}$	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

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 4d shows the overall kinetic processes that were observed with GAC used in this study that included three linear zones. As was 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).

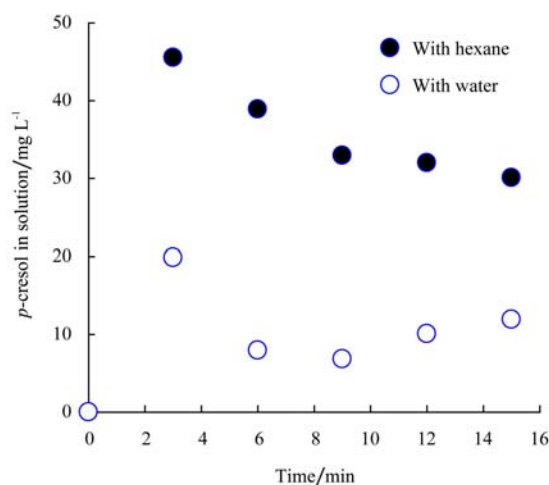
The rate of adsorption decreased as *p*-cresol reached the mesopores and further decreased as the diffusional processes were limited perhaps due to smaller size of micropores than the size of *p*-cresol molecule (6.6 Å X 4.3 Å) (Huang, 2008). Furthermore, the curves did not pass through the origin and 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.

In addition, results from desorption experiments revealed that 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 were 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.

3.9 Effect of solvent

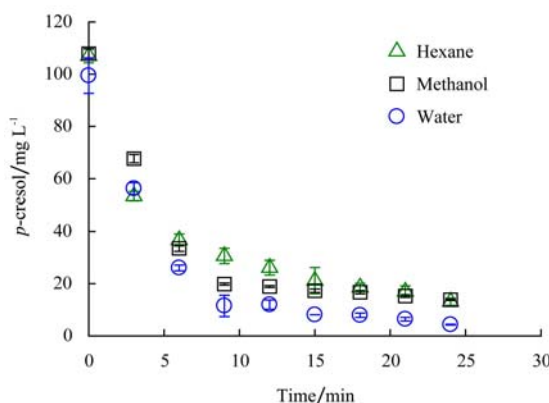
Effect of solvent on adsorption was studied by using

water, methanol, and hexane as solvents in batch experiments at 25°C and adsorbent dose of 20 g L⁻¹. It was found that there was no significant difference ($p=0.602$) (Figure 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 on solvent for adsorption of *p*-cresol by GAC makes it quite suitable for practical application in swine lagoons.



Note: Experimental conditions: Temperature: 25°C, pH: 5.8, and adsorbent dosage: 20 g L⁻¹

Figure 5 Desorption of *p*-cresol from GAC into water and hexane



Note: Experimental conditions: Temperature: 25°C, pH: 5.8, and adsorbent dosage: 20 g L⁻¹

Figure 6 Effect of solvent on adsorption of *p*-cresol on GAC

3.10 Possible mechanism of adsorption

The Brunauer–Emmett–Teller (BET) surface area of the GAC was found to be 662 m² g⁻¹. However, after treatment with H₂SO₄ the surface area decreased to

159 m² 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 spectroscopic analysis of GACA and GAC are shown in Figure 7 A and B respectively.

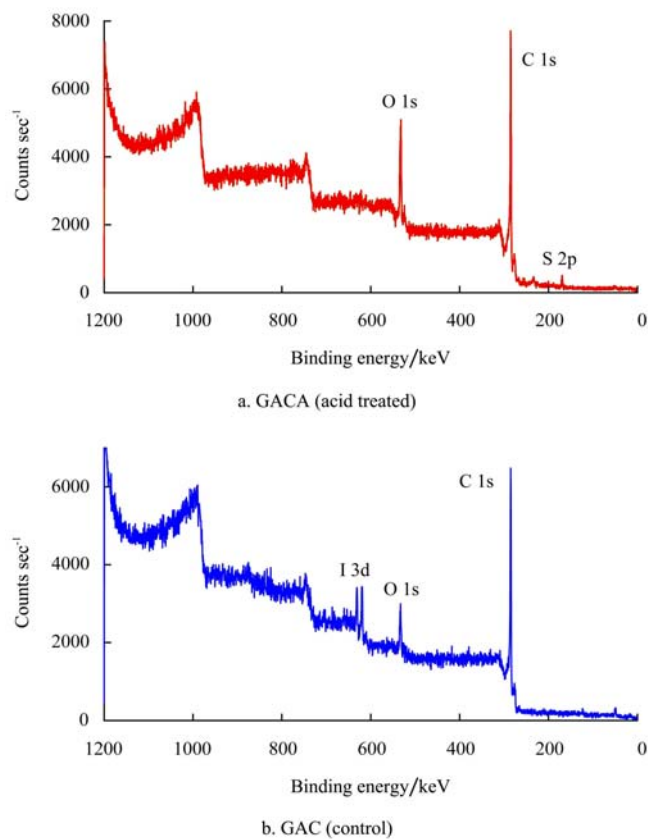


Figure 7 XPS spectra of GACA and GAC

The data showed significant increase (58%) in surface oxygen concentration (Figure 7a) after acid treatment when compared to control (GAC, Figure 7b). In addition, a small peak (S 2p) at 169 eV (Figure 7a) 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 increased in oxygen was also confirmed by the decrease in the acid values of GAC from 8.66 to 1.77 (Figure 8).

When tested, adsorption capacity of GACA significantly decreased when compared to GAC ($p = 0.0006$). Figure 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.

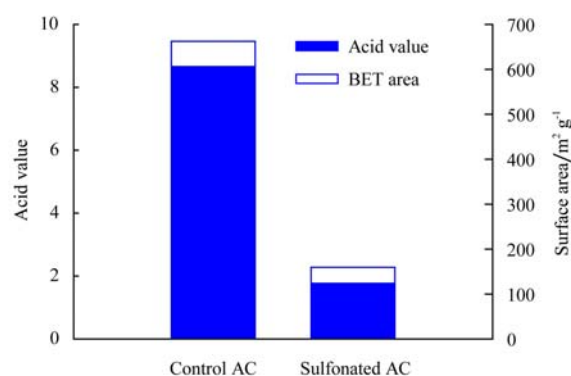
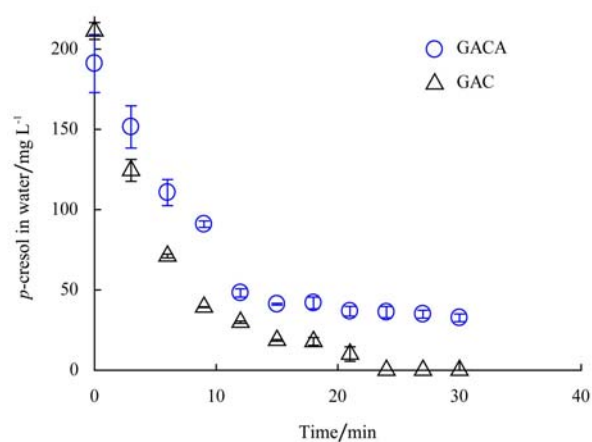


Figure 8 Acid value and specific surface area of GAC and GACA



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

Figure 9 Adsorption of *p*-cresol on GAC and GACA

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-oxidized 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 (1968)'s 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, the 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 Equation (8) and the data presented in Table 3, one can estimate the mass of adsorbent needed for adsorption. For example, for a 1,000 L mixed water system containing 100 mg L⁻¹ of *p*-cresol at 15°C that follows a Freundlich's model, the mass of adsorbent may be expressed as Equation (10):

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

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 Equation (11):

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

where, C_0 is the initial concentration of *p*-cresol (e.g., 100 mg L⁻¹), C_t is the required final equilibrium concentration, and V is the volume of the water to be treated (e.g., 1,000 L).

The simulated results of the example above are shown in Figure 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.

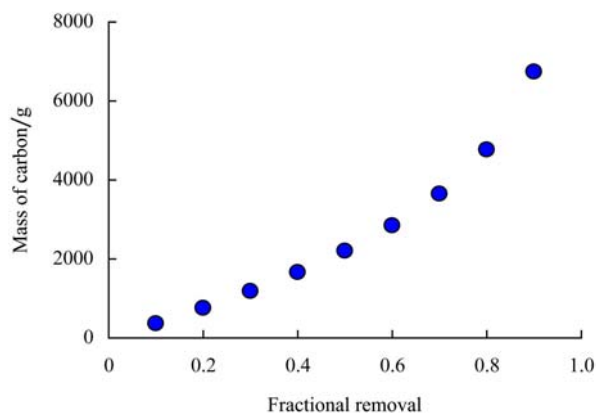


Figure 10 Simulated plot for estimation of adsorbent dosage for mitigation of *p*-cresol (100 mg L^{-1})

4 Conclusion

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 study, 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} . Effects of temperature and pH were found to be not significant and a maximum theoretical adsorption capacity of 68 mg g^{-1} was obtained at the temperature of 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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