

Effect of dissolved oxygen on the adsorptive capacity of a granular activated charcoal for phenol and O-Cresol

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Civil Engineering

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Abstract

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Experimental results show that the presence of molecular oxygen increases the adsorptive capacity of GAC upto 167% for phenol and 141% for o-cresol. These results were signified statistically using SAS program. It is experimentally proved that the biological activity was not responsible for the increased adsorptive capacity of GAC for phenol and o-cresol. Therefore, a chemical reaction is responsible for this increase.

Effect of Dissolved Oxygen on the Adsorptive
Capacity of a Granular Activated Charcoal
For Phenol and O-Cresol

by

Muhammad Subhi AbdulHadi Al-Aama

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF ENGINEERING

In

CIVIL ENGINEERING

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Al-Aama, Muhammad Subhi Abdulhadi, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1992

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BY

MUHAMMAD SUBHI ABDULHADI AL-AAMA

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**KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
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This MASTER OF ENGINEERING REPORT written by MUHAMMAD SUBHI ABDULHADI AL-AAMA under the direction of his Advisor and approved by the Report Committee, has been presented and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the Degree of MASTER OF ENGINEERING.


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To My Parents

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THESIS ABSTRACT

Name of Student: MUHAMMAD SUBHI ABDULHADI AL-AAMA

Title of Study: EFFECT OF DISSOLVED OXYGEN ON THE ADSORPTIVE CAPACITY OF A GRANULAR ACTIVATED CHARCOAL FOR PHENOL AND O-CRESOL.

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This study is an experimental evaluation of the effect of molecular oxygen on the adsorptive capacity of granular activated carbon (GAC) at bench scale. Adsorption isotherm studies were performed for phenol and o-cresol under room temperature (23°C) and controlled neutral pH. Standard bottle-point technique was used for three identical sets of bottles with modifications. A new procedure for obtaining the isotherm, denoted as oxic procedure, is introduced where molecular oxygen is purged in one bottle set. The second set, denoted as anoxic, include purging nitrogen gas for excluding the oxygen. The last set dose not include any purging and only the standard procedure, aerobic, is used.

Experimental results show that the presence of molecular oxygen increases the adsorptive capacity of GAC up to 167% for phenol and 141% for o-cresol. These results were signified statistically using SAS program. It is experimentally proved that the biological activity was not responsible for the increased adsorptive capacity of GAC for phenol and o-cresol. Therefore, a chemical reaction is responsible for this increase.

MASTER OF ENGINEERING DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran 31261, Saudi Arabia

خلاصة الرسالة

أسم الطالب / محمد صبحي عبد الهادي الأعمى

عنوان الرسالة : تأثير الأوكسجين على السعة الإمتزازية للكربون الحبيبي المنشط
للفينول والأرثوكريسول

التخصص الرئيسي : الهندسة المدنية

تاريخ الحصول على الدرجة : مايو ، ١٩٩٢م

خلاصة

هذه الدراسة هي تقييم معلمي لتأثير غاز الأوكسجين الجزيئي على السعة الإمتزازية للكربون الحبيبي المنشط بقياس تجريبي . لقد عملت دراسات عملية الإمتزاز ثابتة الحرارة للفينول والأرثوكريسول تحت درجة حرارة الغرفة العادية (٢٣°س) والرقم الهيدروجيني المتعادل المراقب. أستعملت تقنية الزجاجة - النقطة المعيارية لثلاث مجموعات متماثلة الزجاجات مع إدخال تعديلات . لقد وضعت طريقة جديدة للحصول على عملية الإمتزاز ثابتة الحرارة سميت بالطريقة الأوكسجينية تتطلب ضخ غاز الأوكسجين في زجاجات المجموعة الأولى ، بينما المجموعة الثانية من الزجاجات سميت باللا أوكسجينية ، تتضمن طرد الأوكسجين من زجاجات المجموعة بواسطة ضخ غاز النيتروجين فيها ، أما المجموعة الأخيرة من الزجاجات لا تتضمن ضخ أي غاز ، والعمليات المعيارية فقط قد أستعملت فيها وتسمى الهوائية .

النتائج التجريبية أظهرت أن وجود غاز الأوكسجين الجزيئي زاد السعة الإمتزازية للكربون الحبيبي المنشط لحد ١٦٧٪ للفينول و ١٤١٪ للأرثو-كريسول . هذه النتائج حلت إحصائيا بالكمبيوتر بواسطة برنامج الإحصاء الآلي (ساس) وبينت على أنها حقيقية وليست نتيجة أخطاء عشوائية أو تجريبية . وثبت أيضا بالتجربة أن النشاط الحيوي ليس مسئولاً عن الزيادة في السعة الإمتزازية للكربون الحبيبي المنشط ، وأن تفاعلا كيميائيا هو المسئول إذن عن هذه الزيادة .

درجة الماجستير في الهندسة
جامعة الملك فهد للبترول والمعادن
الظهران - المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

The increasing awareness of the potential hazardous of man-made chemicals and petrochemicals and stringent standards enacted by regulatory agencies, and with increasing concentrations of organic compounds caused by domestic and industrial wastes have been appreciated in the last decade. Most of those chemicals had found difficulty in treatment by conventional biological methods [13]. So today's treatment goals are focused on individual chemicals, rather than gross parameters such as BOD, TOC, etc. Thus the treatment technologies have to be developed and designed towards these chemical-specific standards and goals. Therefore many researchers have been concentrating on the treatment of wastewaters by physical and chemical methods.

Adsorption, which involves the interphase accumulation of substances, is a very efficient physical-chemical treatment method to remove those chemicals out of liquid solution or reduce their liquid phase concentrations to below the inhibition levels, thus permitting the

utilization of the biodegradable constituents of the wastes. Carbon adsorption is one of the best adsorbents, and is widely used today in water, wastewater, and hazardous wastes treatment due to its excellent adsorptive capacity [33,34], and its superior microbial attachment properties [24]. Activated carbon has been used in aerobic reactors [32], and in anaerobic reactors [8,9,31], as well as treatment of surface waters [30].

There was no research to study the effect of oxygen on the adsorptive capacity of carbon, with the exception of Vidic et al. [35], who studied the adsorption process under two conditions of oxygen. This research, that was conducted before the research of Vidic et al was published, will study the effect of oxygen on the adsorptive capacity of granular activated carbon (GAC) under three conditions of oxygen: oxic, aerobic and anoxic by conducting adsorption isotherms taking phenol and o-cresol as typical adsorbates. Phenol and o-cresol are taken since they are common effluents from many petroleum and petrochemical industrial wastewaters, they are priority pollutants and they are extensively found in the literature as to make comparison.

The isotherm data (which represents the equilibrium at constant temperature between the quantity of adsorbate retained per unit mass of adsorbent “q”, and the concentration of adsorbate in solution “C”) are most commonly obtained using the standard bottle-point technique. This technique involves adding a stock solution of adsorbate to different

amounts of activated carbon and mixing until equilibrium is reached and has been widely used in the literature [7,20,21,30,35,37,38] and is used in this study. Unfortunately, a unified procedure for conducting this experiment has not yet been established. So we see diversity in published data because experimental procedures differed with respect to carbon preparation, carbon particle size, volumes of the bottles used in the experiments, volume of adsorbate solution added, buffer application, and equilibration time. The equilibrium time allowed to reach capacity is the most important factor that affects the isotherm data, and it varies from few hours to several weeks [5,25].

The objective of this research is summarized as follows:

- 1) to investigate the equilibration time of phenol adsorbate on granular activated carbon.
- 2) to investigate the effect of dissolved oxygen on the adsorptive capacity of granular activated carbon for phenol and o-cresol.

CHAPTER 2

LITERATURE REVIEW

Giusti et al. [6] studied the removal of residual organic compounds from wastewater by activated carbon adsorption. They have found in their study of adsorptive capacity trends of compounds below four carbons in the chain are: undissociated organic acids > aldehydes > esters > ketons > alcohols > glycols. On the other hand, they found in the trend of the compounds above four carbons that the alcohols have moved ahead of the esters. Also they found that from equilibrium test the ultimate capacity for carbons in batch system is higher than that in continuous system.

Martin and Al-Bahrani [14] observed the effects of solution pH and concentration, carbon particle size, carbon bed depth, and flow rate on the adsorption capacity of GAC by using both batch and column bed systems for pyridine, 2-methylpyridine, and o-cresol. Insignificant effect of carbon particle size on the adsorption capacity of the carbon was found. An increase in pH from 6.8 to 9.5 had no effect on the adsorption capacity but decrease in pH from 6.8 to 5.0 resulted in a significant decrease in adsorption capacity. It is found also that the rate

of adsorption on carbon increased with a decrease in carbon particle size and with increase in initial solution concentration.

Eldib and Badawy [4] reported a considerable amount of data on the adsorption of benzene, toluene, o-xylene, and ethylbenzene on granular activated carbon. The adsorption increase in the order: o-xylene > ethylbenzene > toluene > benzene. Adsorption of the studied compounds increase as their solubilities decrease and molecular weights increase. After a contact time of two days, adsorption at equilibrium concentrations is established.

Peel and Benedek [25] studied the effect of equilibrium time on the activated carbon adsorption of phenol and o-chlorophenol, and stated that the variations in the adsorption capacity in the literature before occur only if true equilibrium is not reached, also reported that the type of buffer used, the carbon particle size, and the initial adsorbate concentration had no effect on the adsorption isotherms. They suggested thirty days equilibration time for GAC and five days for PAC.

Van Vliet et al. [33,34] compared the performance of two activated carbons and eight synthetic adsorbents on the phenol, p-toluene-sulfonate, and p-chlorophenol in terms of adsorption capacities and mass transport properties of the adsorbents. They have found that the activated carbons are superior, however, at high industrial concentrations > 1000 mg/l⁻¹, the adsorption capacities appeared to converge.

McGuire and Suffet [16] studied the interaction between chlorine and activated carbon using a group of four organic compounds which span the range of polarity. The equilibrium adsorption capacities of four polarity probes; nitromethane, methyl ethyl ketone, n-butanol, and 1,4-dioxane; were significantly reduced because of surface oxidation of chlorine. From the kinetic studies conducted it was found that twelve days of equilibration time is sufficient for nitromethane and methyl ethyl ketone and one day for n-butanol and 1,4-dioxane. It is also reported that column studies have been conducted for both oxidized and virgin carbon samples, and showed a significant decrease in the adsorption capacity of activated carbon for an increase in the amount of chlorine reduced on the carbon surface. The nonpolar, virgin carbon surface was shown to be the most efficient surface adsorbent.

Seidel et al. [29] studied the phenol adsorption capacity on four types of activated carbon. The Filtrasorb 400 carbon onto phenol adsorption capacity has distinctly higher capacity than the other carbons. Also the study reported at higher temperature more phenol is adsorbed than at lower temperature. The equilibrium was established after two weeks for all the types of carbon.

Yonge et al. [38] have done an experimental studies for the effects of irreversible adsorption of single solute on GAC. The sorbates were five low molecular weight substituted phenols. The study concluded that a significant fraction of adsorption on GAC was found to

be irreversible, and the occurrence of irreversibility influence the shape of the isotherm. They noted that a sufficient limit for equilibrium time was ten days.

Najm et al. [20] studied the removal of trichlorophenol (TCP) on powdered activated carbon (PAC) by running equilibrium and batch kinetic tests. Trichlorophenol isotherm bottles were incubated for seven days. Isotherm tests in groundwater showed significant reduction (50%) in adsorption capacity because of the decrease in equilibrium capacity. The presence of naturally occurring humic substances in groundwater was found to significantly decrease the PAC capacity and rate of adsorption of TCP.

Speth and Miltner [30] did isotherms studies of activated carbon by using three types of water, distilled-deionized (DD) water, sand filtered Ohio river (OR) water, and sand filtered Great Miami Aquifer (GMA) water. They have found that the natural water isotherms generally had a reduced capacity compared with the DD water isotherm.

Vidic et al. [35] examined the influence of molecular oxygen on the adsorptive capacity of GAC for phenol, o-cresol, and 3-ethylphenol. It was found that two weeks of equilibration time is sufficient. They introduced a new experimental procedure for obtaining adsorption equilibria data, denoted as anaerobic, providing elimination of molecular oxygen with the adsorption process. It was found that the capacity of GAC under aerobic conditions is greater than the capacity under

anaerobic conditions especially in the low concentrations. The difference at higher concentrations tends to be small.

Nakhla et al. [21] studied the impact of nitrogen on the adsorptive capacity of activated charcoal for phenol. Ten days equilibrium time was used. It was shown that the capacity of activated charcoal with nitrogen purged solution is lower than that with nitrogen free solution by as much as fifty percent.

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 Materials and Equipments

The materials and equipments used in all the experiments conducted in this study are:

- 1) Granular activated carbon (GAC) : the activated carbon used in this study was mesh activated carbon supplied by the manufacturer (BDH Chemicals Ltd., Pode, England) in a 10×40 U.S. mesh size. To produce more uniform size ranges, carbon was sieved to the 10×12 and 12×14 U.S. mesh sizes. Before usage, the carbon was washed several times with water until all the fines in it were removed. The carbon was then dried in an oven at 108°C for one day, and finally stored in a desiccator prior to use. All the adsorption experiments were performed with this batch of GAC.
- 2) Buffered water : deionized water was buffered at neutral pH by the addition of 0.01 moles of potassium phosphate mono basic (KH_2PO_4) per liter of deionized water. The pH was then adjusted

to 7.0 by the careful addition of NaOH and/or HCl solutions. This water was used for the preparation of all the organic and standard solutions.

- 3) A 1000 mg l^{-1} phenol solution was prepared by dissolving 1g of reagent grade phenol per liter of buffered water.
- 4) A 1000 mg l^{-1} o-cresol solution was prepared by dissolving 1g of reagent grade o-cresol per liter of buffered water.
- 5) 160-ml glass bottles with rubber caps.
- 6) Standard glass wares and glass tubes.
- 7) 0.45 microns millipore filter paper (diameter=0.5 in.).
- 8) Pausch & Lamb mass spectrophotometer.
- 9) Oxygen and Nitrogen gas cylinders.
- 10) D.O. probe to measure the dissolved Oxygen.

3.2 Adsorption Equilibria

To conduct the isotherm experiment for any adsorbate a contact period, or time to reach equilibrium, between the GAC and the adsorbate is the most important factor. There are two techniques to determine the time required to reach equilibrium, batch technique, and standard bottle point technique. The two techniques are described as follows:

3.2.1 Batch Technique

Powdered activated carbon (PAC) is the carbon most suitable for the batch-type contact process. The experiment is carried by adding a

known quantity of carbon to a given volume of the water to be treated and mixing until true mixture is observed. The mixture is then placed in a stirring apparatus. A sample is then removed at various time intervals from which the carbon is immediately removed either by filtration or centrifugation. The residual concentration of the contaminant is subsequently determined in each sample. The data are plotted to show the change in concentration with time. Adsorption equilibrium is achieved at the contact periods where no significant change in concentration is observed with increased time.

This technique has a disadvantage in which it assumes true mixture is achieved as samples are subsequently drawn while it is not always the case. Samples may be drawn from parts of the mixture that could have relatively different residual concentrations of the adsorbate.

3.2.2 Standard Bottle Point Technique

GAC is used in this technique. The technique involves placing accurately weighed equal amounts of GAC into a series of bottles having equal volumes of adsorbates. After placing them in a shaker, bottles are removed at various time intervals one at a time and tested as explained earlier in the batch technique. This technique involves neither change in the volume of adsorbate, nor change in the amount of carbon for each sample tested. Therefore, it is considered more accurate than the batch technique and yet, more simple. The standard bottle point technique is

used, therefore, in this study for the equilibration time experiment and for the isotherm test experiments as presented below.

3.3 Equilibration Time for Phenol

Twenty of the 160-ml bottles were prepared. Then 100 ml from the phenol solution was filled in each bottle using volumetric pipet. Subsequently 0.5g of GAC was accurately weighed (± 0.1 mg) and put in each bottle. The bottles were closed with rubber caps and placed in a shaker at room temperature (23°C) for a period of ten days. Two bottles were removed from the shaker every day where 20 ml samples were withdrawn from each bottle, filtered through 0.45 μ m Millipore filter paper, and analyzed for phenol.

A spectrophotometer was used to measure the adsorbate concentration at a wave length of 270 nm for phenol. Dilution by buffered water was made when needed. Calibration curve was constructed for phenol and used to convert absorbance readings to concentrations.

This generated two sets each of 10 bottles. The set which showed the better results was presented in this report.

3.4 Isotherm Tests

As previously mentioned, the bottle-point technique was used for the adsorption isotherms tests. However, three different procedures;

denoted henceforth as oxic, aerobic, and anoxic; were employed in conducting these tests.

The oxic procedure required full saturation of the sorbate with molecular oxygen. This involves pipetting 100 ml of sorbate solutions into a series of 160-ml bottles. Then each bottle was purged with oxygen gas for four minutes inside the solution and two minutes in the head space of the bottle and quickly closed with a rubber stopper.

The aerobic procedure is the traditionally used technique that is similar to the oxic procedure but no purging is done. This procedure allows for three different sources of molecular oxygen in the bottles, air in the headspace of the bottles, air associated with the carbon particles, and dissolved oxygen present in the solution water. The dissolved oxygen for one bottle was measured by D.O. probe.

While the anoxic procedure, in the other hand, requires the absence of molecular oxygen from isotherm bottles. This was achieved by purging the bottles as the oxic procedure but using nitrogen gas. From previous experience it has been shown that this purging time is enough to reduce the dissolved oxygen concentration to almost zero [21].

In each set of bottles, one bottle was left without GAC. This bottle served as a blank to check for sorbate volatilization and/or adsorption onto the walls of the bottle during the equilibration period.

All the isotherm bottles were then placed in a shaker at room temperature (23°C) and allowed to equilibrate for ten days. After ten

days, the bottles were removed from the shaker and decapped. A 20-ml sample was drawn from each bottle and filtered through 0.45 μm Millipore filter paper of 0.5 in. diameter. The filtrates were stored in 30-ml clean glass vials before analysis.

Prior to the analysis of the samples on the mass spectrophotometer, a calibration curve for phenol and o-cresol was generated by running 10, 20, 30, 50, 70 and 100 mg l^{-1} standard solutions of each compound prepared from the original solutions on the mass spectrophotometer. The wave length used for phenol and o-cresol detection was 270-nm. In both cases a 1 cm quartz cell was used.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Phenol Equilibrium Time.

The results of the phenol equilibration data vs. time in days were presented in Table 4.1 and drawn in figure 4.1. From the given table and figure, it can be seen that two rates of phenol adsorption exist. The first rate is associated with rapid decline in the concentration of phenol that occurs in the first day. Particularly, the phenol concentration declined from 1000 mg/l to about 263 mg/l which represents 74% removal in the phenol concentration after the first day. The second rate is slow where in the remaining nine days the phenol concentration went down from 263 mg/l to 144 mg/l that represented about 12% reduction from the initial concentration.

These observations strongly agree with the findings of Peel and Benedek [25]. They described the adsorption behavior of the adsorbate with GAC by a dual rate macropore-micropore adsorption model. They stated that 60% to 80% of the adsorptive equilibrium is reached within few hours, and the remaining capacity is utilized very slowly.

Table 4.1: Phenol Equilibration Time

Time (days)	Concentration (mg/l)
0	1000
1	263
2	232
3	205
4	165
5	208
6	177
7	168
8	146
9	138
10	144

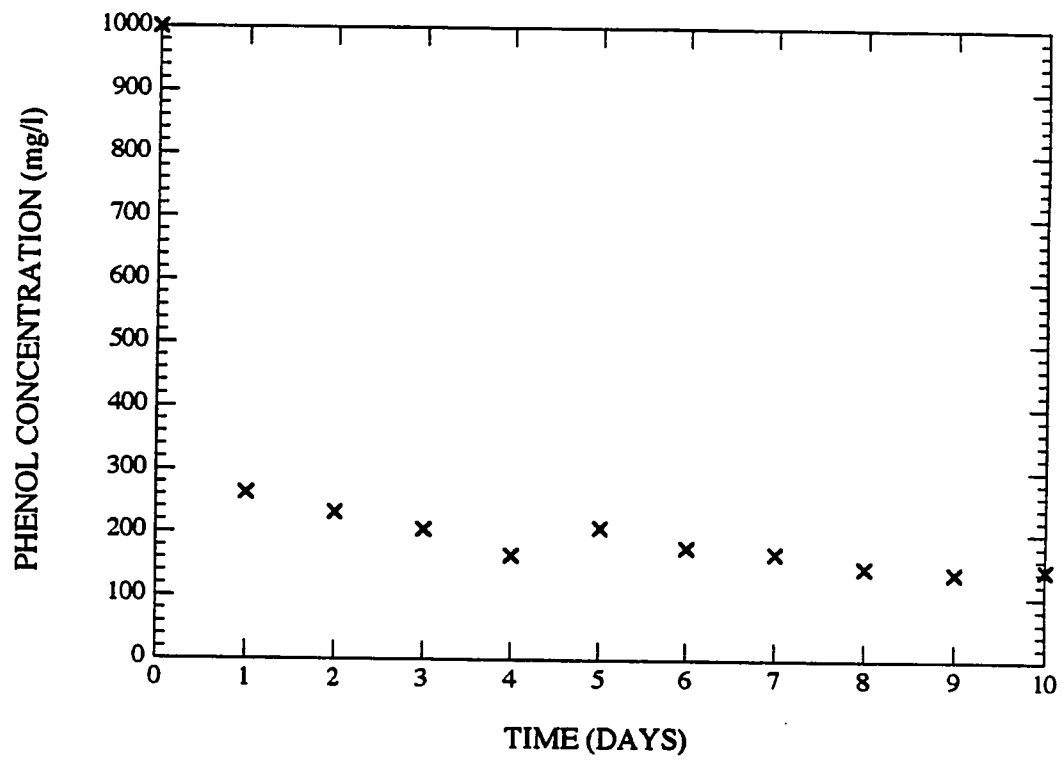


Fig 4.1: Time Equilibrium Curve for Phenol

Also it can be seen that a 10 days period would be sufficient to reach equilibrium as the curve levels out after the eighth day without significant change in the concentration. Particularly the phenol concentration after the eighth day was 146 mg/l while after the tenth day it was 144 mg/l which marks a 2 mg/l decrease in two days (<1% decrease per day). This change is within the spectrophotometer and human errors. This finding strongly agrees with the observation of Yonge et. al. [38], who found that eight days were needed for equilibration and added two days safety factor, resulting in the ten days equilibration period.

The ten days equilibration period for phenol is applied for all o-cresol in this study. The capacity for phenol is less than the capacity of o-cresol, as will be seen later, because o-cresol has more molecular weight and it is less soluble in water than phenol. Therefore, o-cresol is more adsorbable than phenol. o-cresol and phenol belong to the same organic group called aromatics, so it is expected that the diffusion coefficients for both compounds are similar.

4.2 Adsorption of Adsorbates

An extensive study of the effect of oxygen on the adsorptive capacity of GAC was performed using single-solute adsorption isotherms for phenol (PH) and o-cresol (OC). Phenol and o-cresol adsorption isotherm tests were performed at room temperature (23°C)

and neutral pH. Experimental conditions for the isotherm tests conducted are listed in Table 4.2, while the physical-chemical characteristics of the sorbates are listed in Table 4.3.

For both phenol and o-cresol solutions the corresponding carbon load for each liquid phase concentration was calculated according to the following equation

$$q = \frac{V (C_o - C)}{M} \quad (1)$$

where

q = adsorbed phenol (mg/g)

V = liquid volume (l)

M = mass of activated carbon (g)

C_o = initial liquid phase concentration of phenol or o-cresol (mg/l)

C = final liquid phase concentration of phenol or o-cresol (mg/l)

For purpose of simulation to describe the isotherms, two isotherm models are given:

i) Freundlich adsorption model which takes the form

$$q = K C^{1/n} \quad (2)$$

Table 4.2: Experimental Isotherm Conditions at 23°C

Adsorbate	Initial Concentration (mg/l)	Particle Size (U.S. Mesh)	Head-Space	Isotherm Type	Dissolved Oxygen (mg/l)
Phenol	1000	10×12 and 12×14	O ₂	oxic	
	1000	10×12 and 12×14	air	aerobic	6.7
	1000	10×12 and 12×14	N ₂	anoxic	≈ 0
o-cresol	1000	10×12 and 12×14	O ₂	oxic	
	1000	10×12 and 12×14	air	aerobic	7.8
	1000	10×12 and 12×14	N ₂	anoxic	≈ 0

Table 4.3: Physical-Chemical Characteristics of Sorbates

Sorbate	Symbol	Molecular Weight (g)	Solubility (%)
Phenol	PH	94.11	8.45
o-cresol	o-C	108.14	2.5

where q and c were described previously, and K and $1/n$ are the model constants.

ii) Langmuir adsorption model which takes the form

$$q = \frac{Q b C}{1 + b C} \quad (3)$$

where Q is the maximum number of moles adsorbed per mass adsorbent, and b is an empirical constant.

Equation 2 can be linearized by taking the logarithms of both sides of the equation as follows:

$$\log q = \frac{1}{n} \log C + \log K \quad (4)$$

while equation 3 can be linearized in an implicit form as follows:

$$\frac{C}{q} = \frac{1}{Q b} + \frac{1}{Q} C \quad (5)$$

In order to findout which of the two isotherm models represents the data more accurately, the two parameters K and $1/n$ for the Freundlich equation, and the two parameters Q and b for the Langmuir equation were obtained by nonlinear least-square regression analysis. The commonly used SAS program, which is one of the best in the field of statistical analysis, was used to carryout the regression analysis. Langmuir and Freundlich model parameters, correlation coefficients,

and sum of the square errors for the phenol and o-cresol data are presented in the next section

4.2.1 Phenol Isotherm

The calibration curve used for the determination of the phenol liquid phase concentration is depicted in figure 4.2.

Tables 4.4 to 4.6 summarize the results of the relationships between the adsorbed phenol and the equilibrium liquid phase concentration for nitrogen purged, non-purged, and oxygen purged, respectively. It was a good indication that the blank concentration were in a close agreement with that of the phenol stock solution, which means lack of volatility and biodegradation of the adsorbate under the conditions of the experiments. The results are also plotted in figures 4.3 to 4.5 in arithmetic and logarithmic scales to represent the Langmuir and Freundlich equations after excluding the missing values and the odd numbers.

Tables 4.7 and 4.8 list the summary of the SAS programs listings for the regression analysis of Langmuir and Freundlich equations, respectively. From these tables it can be said that phenol isotherms are better described by Langmuir equation than the Freundlich equation in terms of the correlation coefficient (R^2). However, poor distribution of the data is observed along the fitted Langmuir lines shown in figure 4.4,

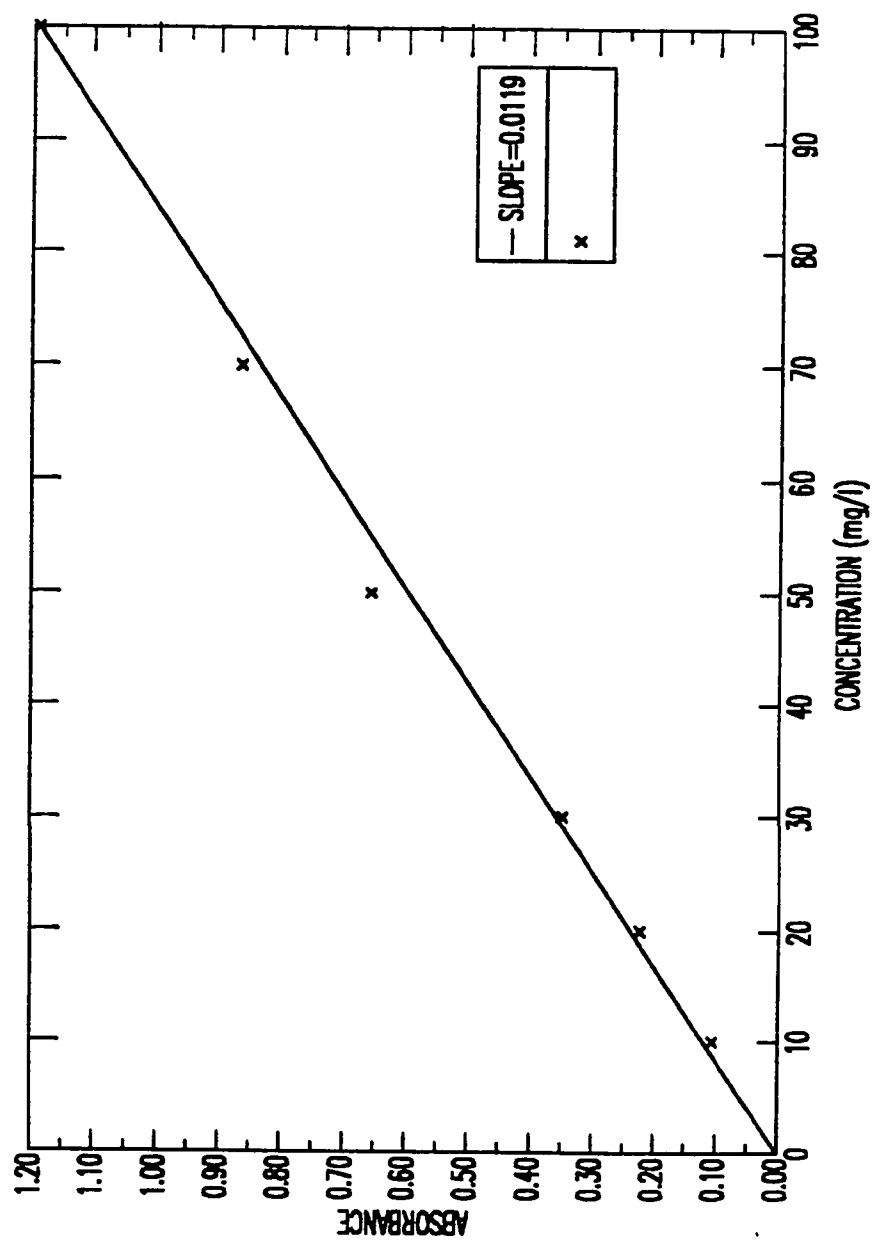


Figure 4.2: Phenol Calibration Curve

Table 4.4: Phenol Isotherm Results under Anoxic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	921.5	
150	-	-
240	511	171.0
370	429	133.0
480	382	112.4
600	194	121.0
750	180	99.0
890	101	92.0
1000	58	86.3
1090	39	81.0
1350	-	-

Table 4.5: Phenol Isotherm Results under Aerobic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	921.5	
150	709	142
240	453	195
370	290	171
480	85	174.3
600	284	106.3
750	64	114.3
890	15	102
1000	11.6	91
1090	8.6	84
1350	3.4	68

Table 4.6: Phenol Isotherm Results under Oxidic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	921.5	
150	654.0	178.3
240	435.0	202.7
370	205.0	194.0
480	134.0	164.0
600	27.3	149.0
750	6.3	122.0
890	3.8	103.0
1000	-	-
1090	1.1	84.5
1350	-	-

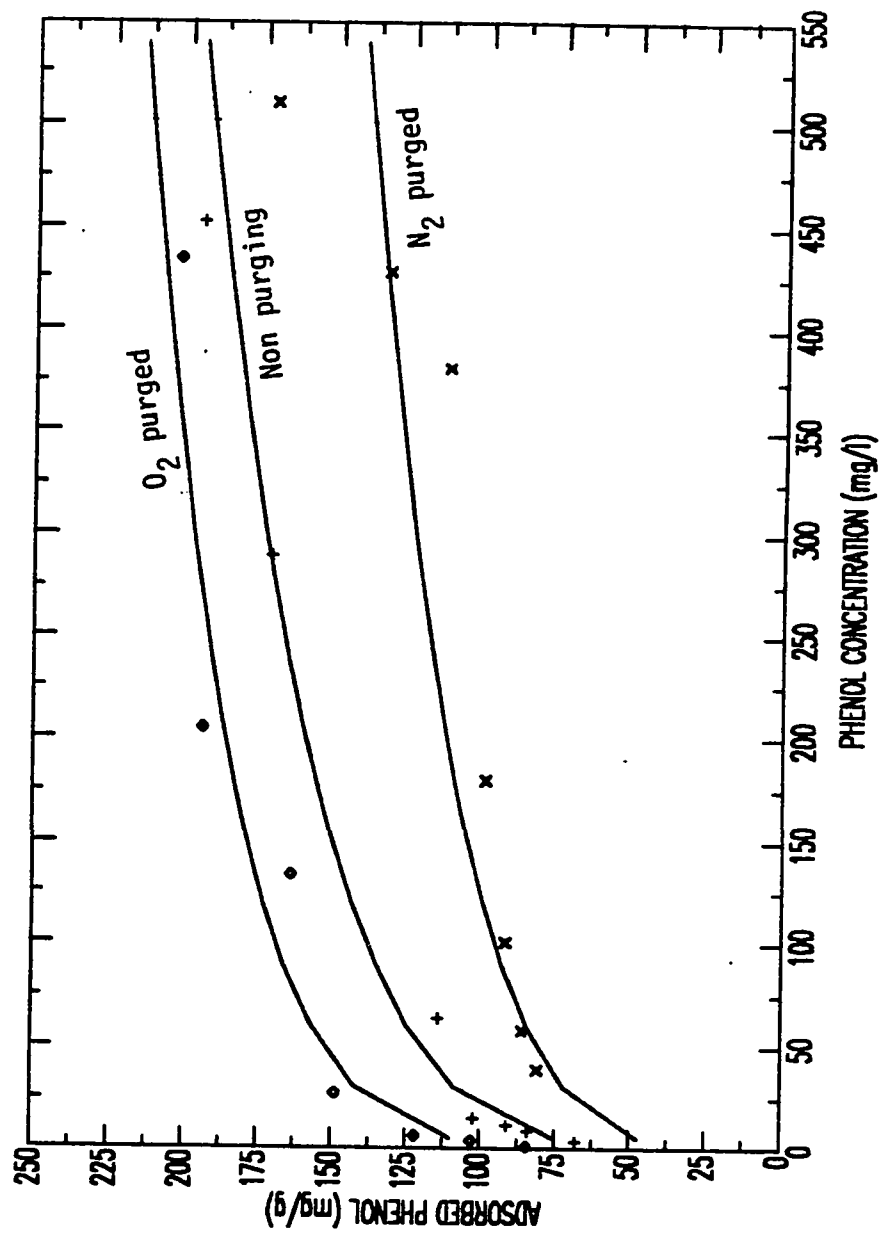


Figure 4.3: Langmuir Phenol Isotherms on Activated Carbon

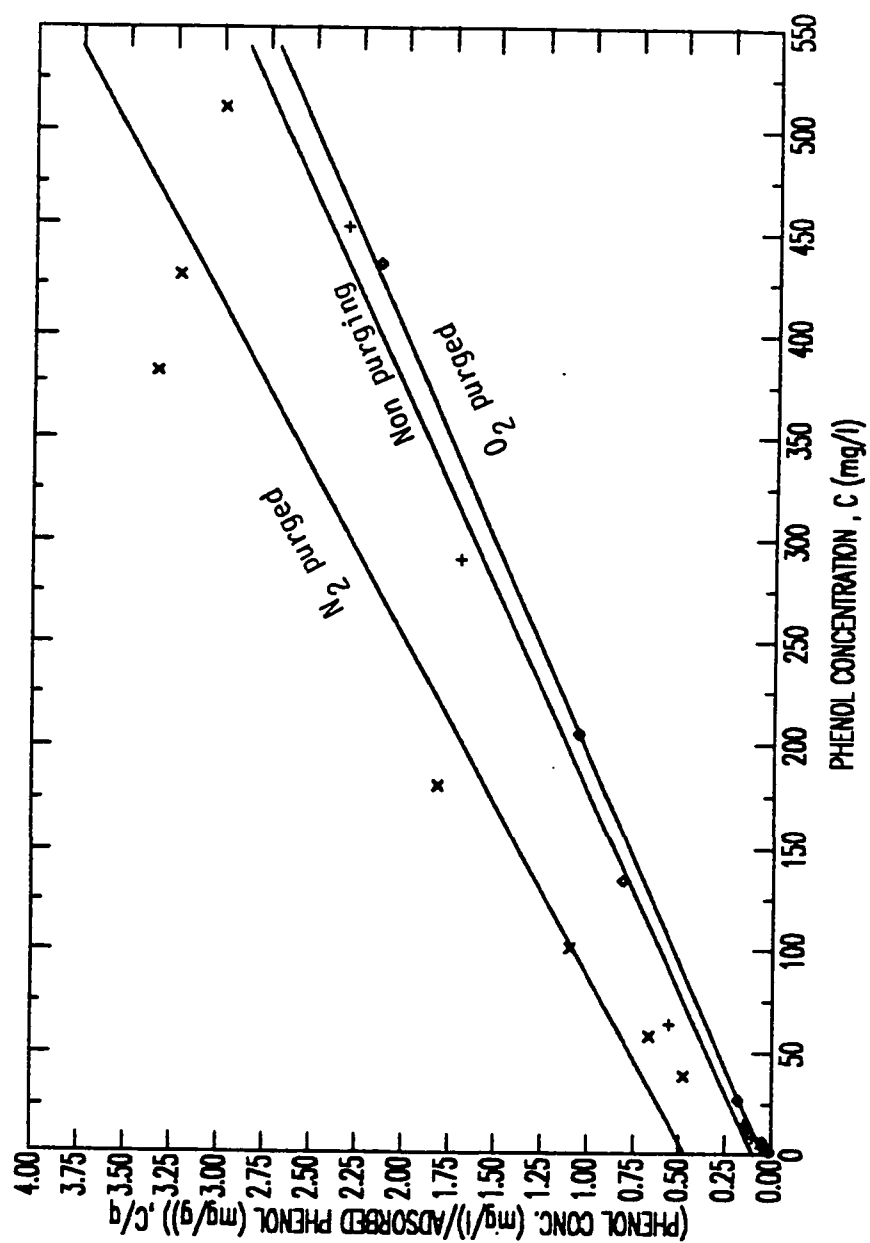


Figure 4.4: Linearized Langmuir Phenol Isotherms

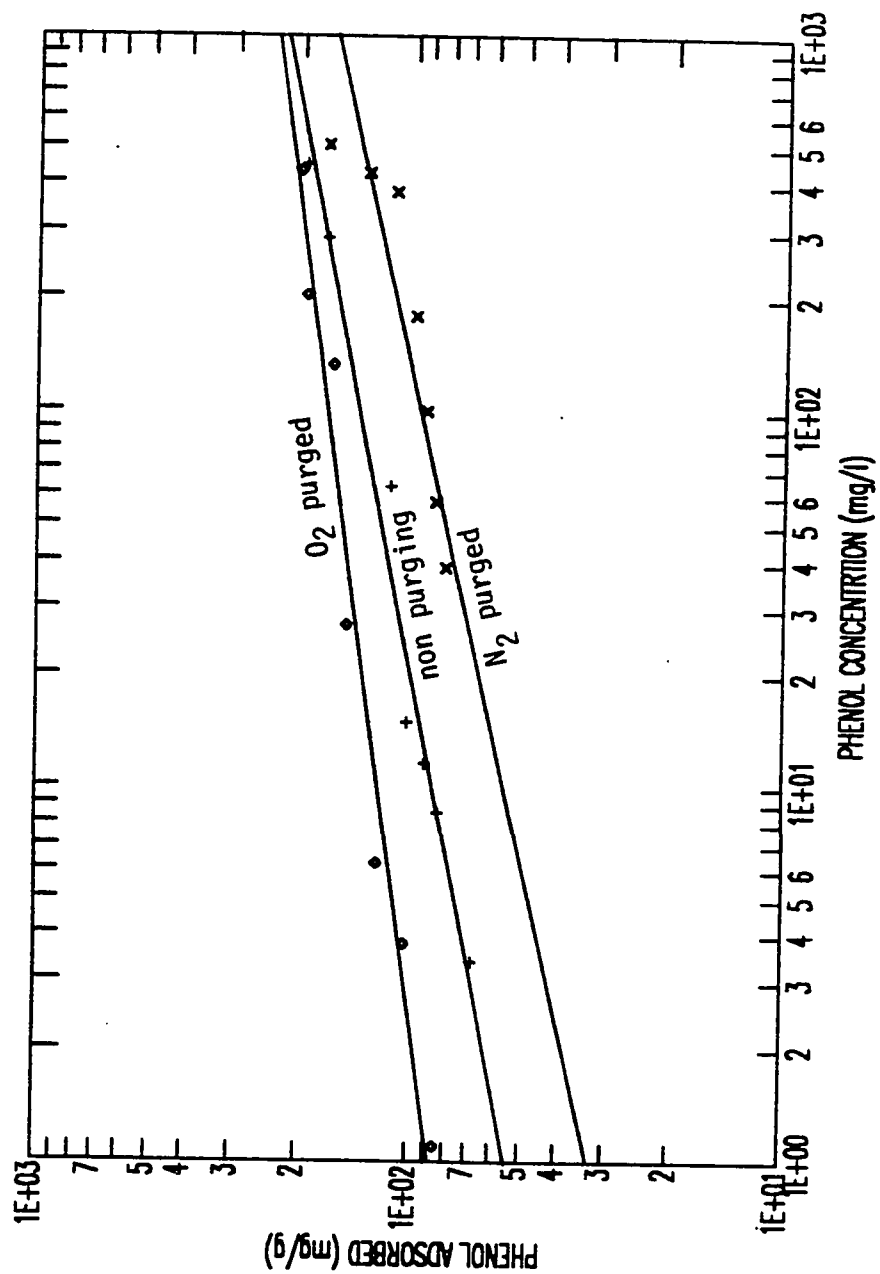


Figure 4.5: Freundlich Phenol Isotherms on Activated Carbon

Table 4.7: Adsorption Model Constants of Langmuir Equation for Phenol

Isotherm Type	Q	b	(R ²)*	SSE**
oxygen purged	203.4	.111	.996	.017
non-purging	195.6	.0524	.991	.0473
nitrogen purged	164.2	.013	.91	.804

* Correlation Coefficient

** $SSE = \sum (\text{Observed value} - \text{Predicted value})^2$

Table 4.8: Adsorption Model Constants of Freundlich Equation for Phenol

Isotherm Type	K	1/n	R ²	SSE
oxygen purged	87.47	.1425	.971	.0035
non purging	54.43	.2027	.978	.0035
nitrogen purged	32.56	.233	.813	.0148

in the other hand, uniform distribution of the data along the fitted Freundlich lines. This results in a lower sum of the squared errors (SSE), where the error is defined as the difference between the observed and the predicted value, by the Freundlich model which agrees with Yonge et. al. [38]. They found that Freundlich equation provided the best description of the phenol isotherm adsorption data as indicated by a lower SSE. Yen et. al. [36] stated that another model called the modified three-parameters Freundlich model is more effective in describing single-solute adsorption than the two models presented, however, the limitation to use this model is due to the difficulty in solving complicated mathematics involved. It is stated at this point that both Langmuir and Freundlich models are valid for describing the phenol isotherm adsorption.

Figures 4.3 to 4.5 indicate the presence of molecular oxygen in the test environment had a strong impact on the adsorptive capacity of GAC for phenol. For the equilibrium concentration of 1000 mg/l, for example, the adsorptive capacity of GAC exhibited under oxic conditions 41% higher than anoxic adsorptive capacity, and 4.3% higher than the aerobic adsorptive capacity. While the aerobic adsorptive capacity is 35% higher than the anoxic adsorptive capacity. These differences in GAC adsorptive capacity are more noticed in the lower concentration. For the equilibrium concentration of 1 mg/l, for example, the oxic GAC adsorptive capacity is 167% higher than the anoxic adsorptive capacity, and 60% higher than the aerobic adsorptive

capacity, while the aerobic adsorptive capacity is 67% higher than the anoxic adsorptive capacity. This is also dictated by the fact that the oxic isotherms had a lower value of $1/n$ in the Freundlich equation. These differences are also noticed from tables 4.7 and 4.8 where the values of K and Q for the phenol isotherms consistently yielded higher capacity for oxic isotherm than aerobic and anoxic conditions. Moreover, higher capacity is observed for the aerobic conditions than for the anoxic conditions. The amount of the molecular oxygen also affected the adsorptive capacity of GAC.

Since identical carbon masses were used for the isotherms (i.e. oxygen purged, non-purged, and nitrogen purged), the differences in capacities is better illustrated by a comparison of the residual liquid phase concentration. Figure 4.6 shows plots of the ratio of the residual concentration to the initial concentration as a function of the carbon mass for phenol. It is evident from the figure that the residual concentration of phenol in the oxygen purged isotherm was consistently lower than the concentration in the non-purged isotherm, and the residual concentration of phenol in the non-purged isotherm was consistently lower than the concentration in the nitrogen purged isotherm. To emphasize on these findings, and to make sure that these differences are not due to experimental errors, statistical analysis was carried out by SAS program using anova procedure (the theory of this procedure is found in Montgomery [18]). The null-hypothesis that

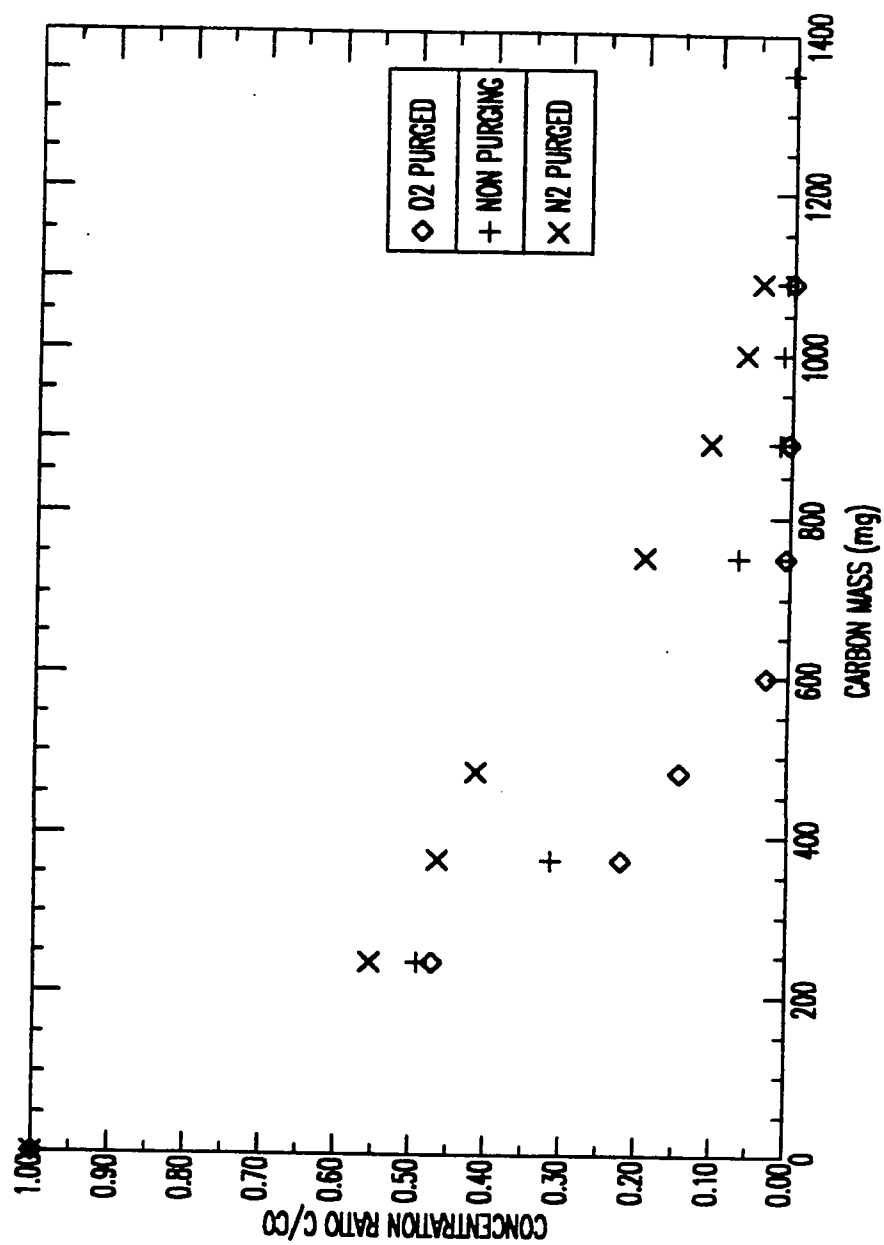


Figure 4.6: Relationship Between Residual Phenol Concentration and Carbon Dosage

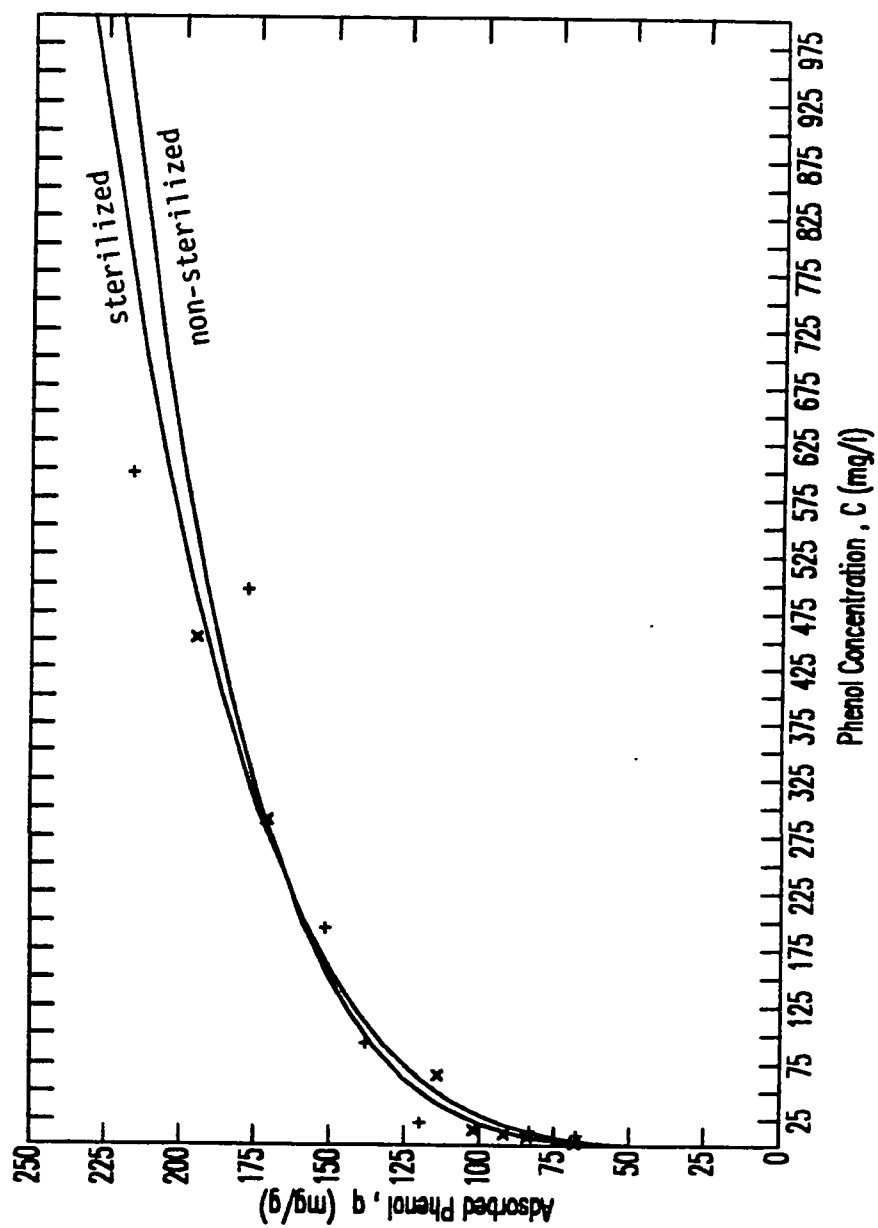


Figure 4.7: Langmuir Sterilized and Non-Sterilized Phenol Isotherms on Activated Carbon

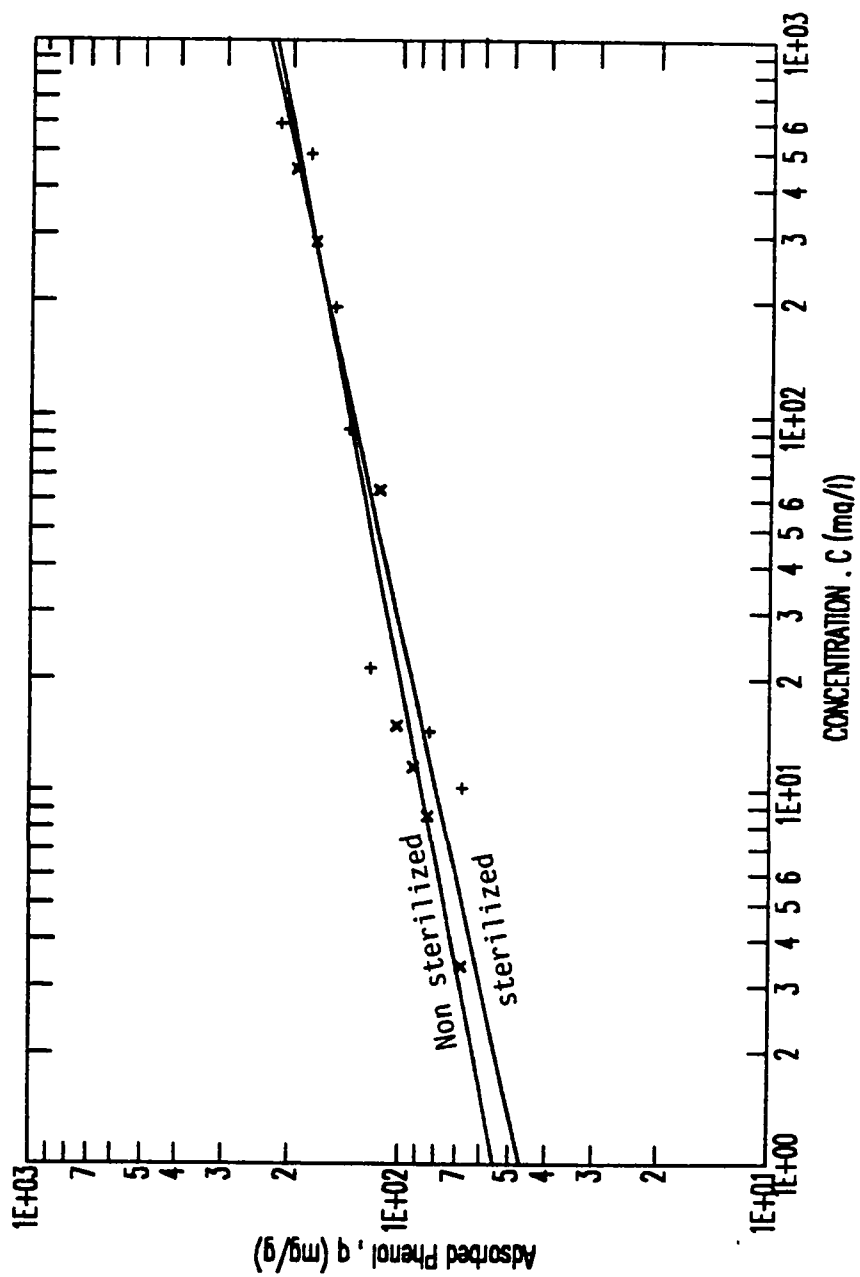


Figure 4.8: Freundlich Sterilized and Non-Sterilized Phenol Isotherms on Activated Carbon

attributes the differences in adsorptive capacities of GAC due to the dominance of oxygen to random errors was tested.

The analysis of variance presented in Appendix 3 clearly show that the null-hypothesis is strictly rejected at α value as low as 0.0009.

The possibility that biological degradation under oxic and aerobic conditions was responsible for the higher observed GAC adsorptive capacities was rejected, by showing that the sterilized phenol isotherm curve obtained coincides well with the non-sterilized phenol isotherm curve. This is depicted in figures 4.7 and 4.8. This rejection was also achieved by Peel and Benedek [25] and Vidic et. al. [35]. Therefore, it is concluded that chemical reaction between the molecular oxygen and the phenol adsorbate catalyzed by the surface of the carbon is responsible for the increase in the adsorptive capacity of GAC.

4.2.2 o-cresol Isotherm

The calibration curve used for the determination of the o-cresol liquid phase concentration is depicted in figure 4.9.

Tables 4.9 to 4.11 show the results of the relationship between the adsorbed o-cresol and the equilibrium liquid phase concentration for nitrogen purged, non-purged, and oxygen purged, respectively. The aforementioned results are plotted in figures 4.10-4.12. As in the case with phenol, it was a good indication that the blank concentration were in a close agreement

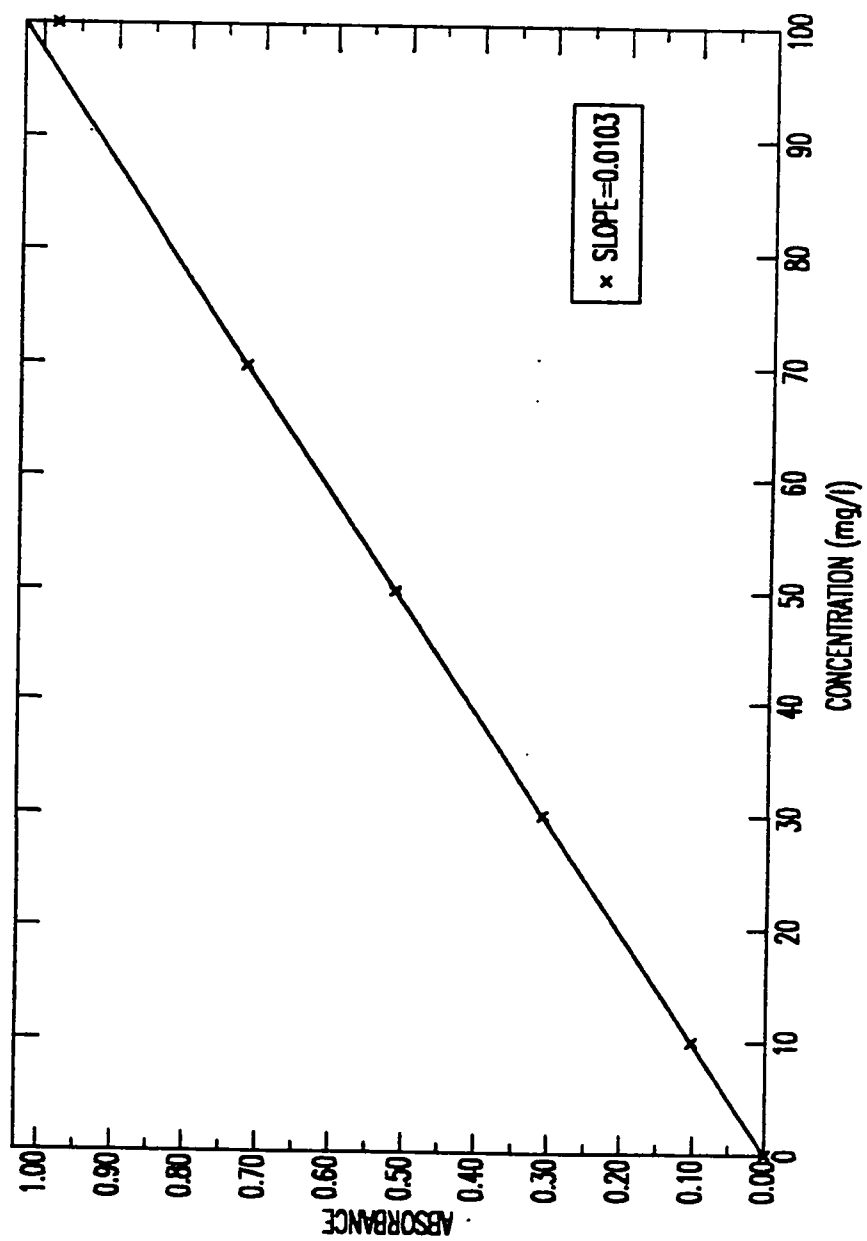


Figure 4.9: o-Cresol Calibration Curve

Table 4.9: o-Cresol Isotherm Results under Anoxic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	906	
100	686	220.0
150	626	186.7
200	509	198.5
250	408	199.2
300	359	182.3
400	225	170.3
500	127	155.8
600	75	138.5
700	40	123.7
1000	11	89.5

Table 4.10: o-Cresol Isotherm Results under Aerobic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	906.0	
100	579.0	327.0
150	461.0	296.7
200	339.0	283.5
250	237.0	267.6
300	155.0	250.3
400	34.0	218.0
500	2.50	180.7
600	1.94	150.7
700	1.60	129.2
1000	1.55	90.5

Table 4.11: o-Cresol Isotherm Results under Oxidic Conditions

M (mg)	C (mg/l)	q (mg/g)
0	906.0	
100	600.0	306.0
150	471.0	290.0
200	368.0	269.0
250	217.0	275.6
300	124.0	260.7
400	8.70	224.3
500	2.30	180.7
600	1.94	150.7
700	1.55	129.2
1000	1.55	90.5

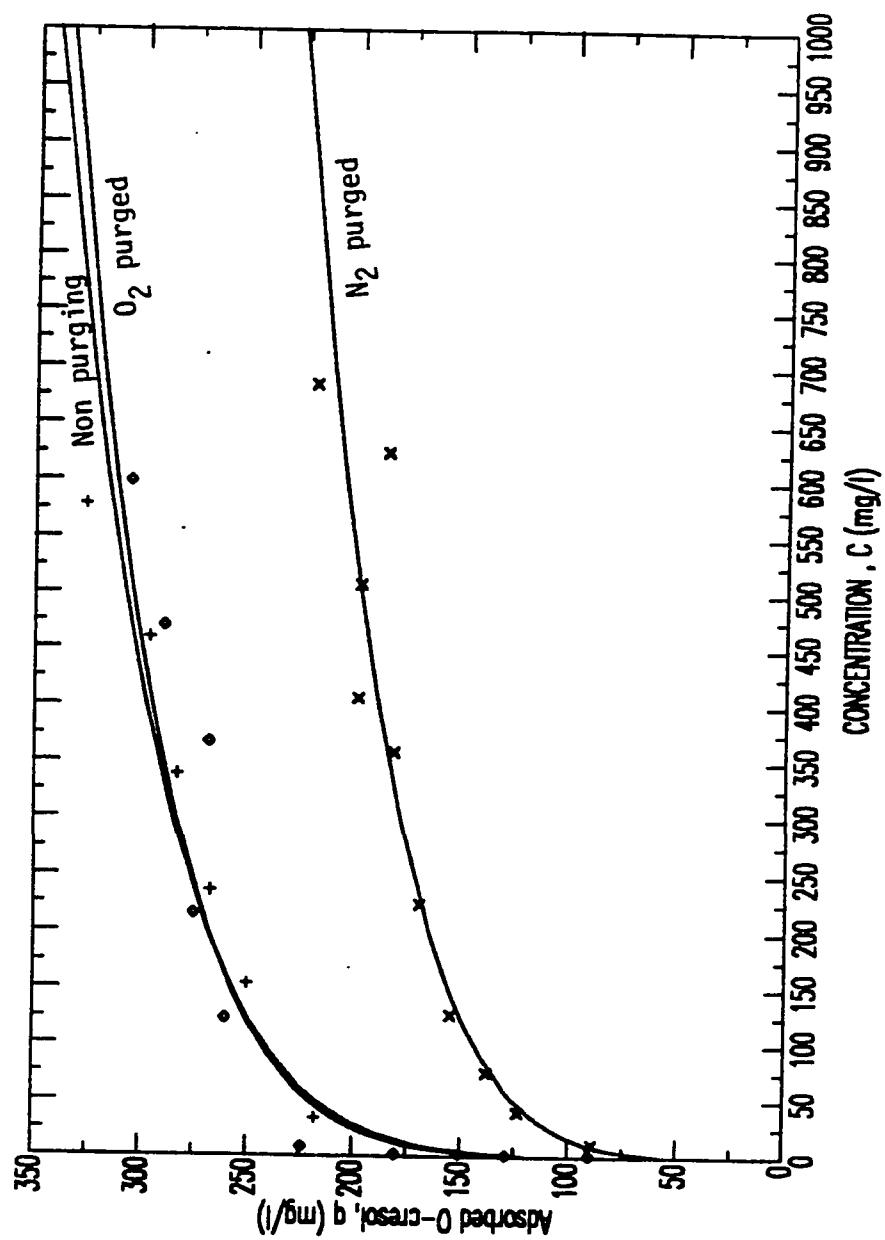


Figure 4.10: Langmuir o-Cresol Isotherms on Activated Carbon

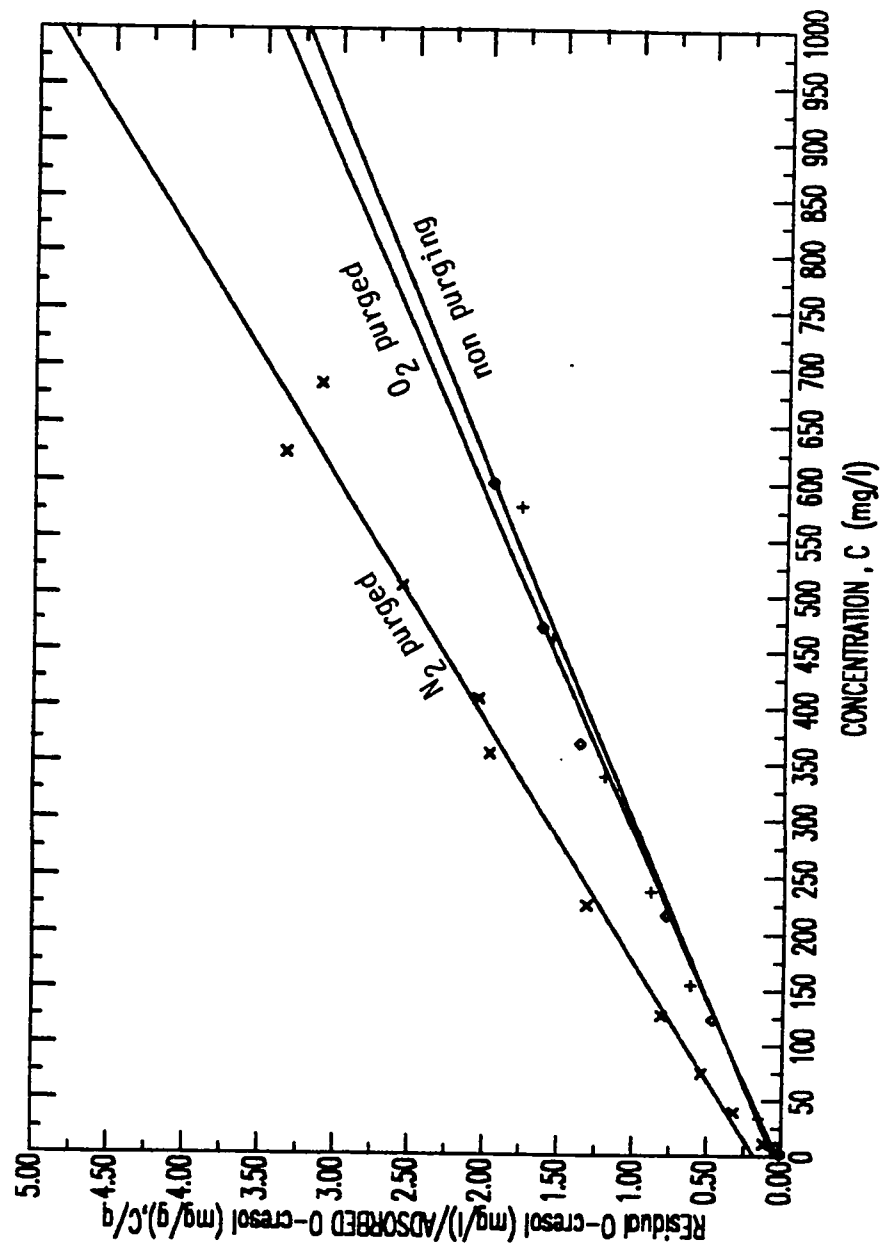


Figure 4.11: Linearized Langmuir o-Cresol Isotherms

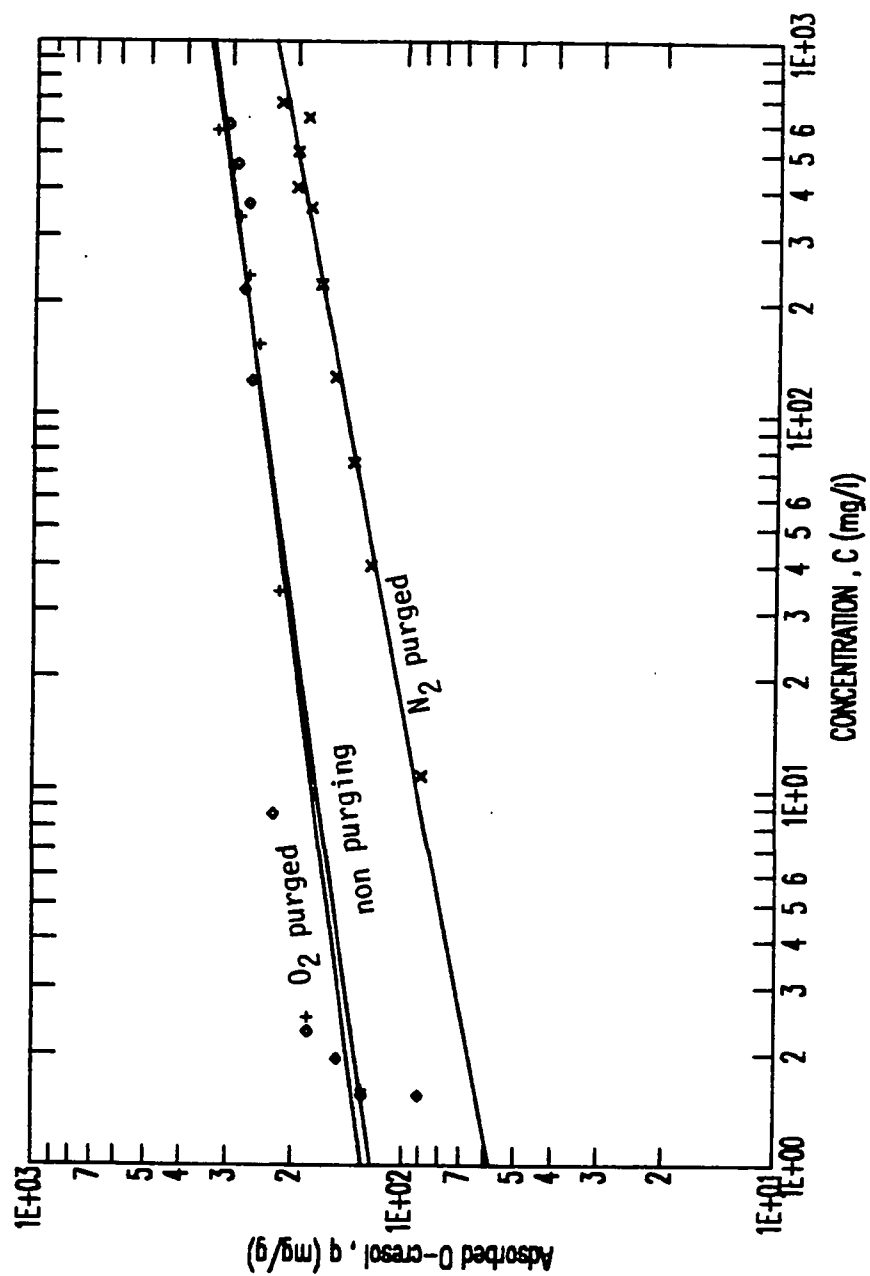


Figure 4.12: Freundlich o-Cresol Isotherms on Activated Carbon

with that of the o-cresol stock solution, which means lack of volatility and biodegradation of the adsorbate under the conditions of the experiments. The results show that o-cresol is adsorbed more than phenol even when the carbon masses are decreased. This is predicted as o-cresol is less soluble in water and has a higher molecular weight (Table 4.3).

Tables 4.12 and 4.13 list the summary of the SAS programs listings for the regression analysis of Langmuir and Freundlich equations, respectively. Like phenol isotherms, o-cresol isotherms are described by Langmuir model in terms of correlation coefficient (R^2), and described by Freundlich model in terms of SSE.

Figures 4.10 to 4.12 indicate that o-cresol isotherms curves under oxic conditions are very close to those of the aerobic conditions. This could indicate that oxygen purging dose not affect the adsorption capacity of GAC for o-cresol under oxic and aerobic condition. However, this statement must be observed with the following two points: 1) the accuracy of the spectrophotometer used was not sufficient in the low concentration range of o-cresol as indicated in Tables 4.10 and 4.11 that give a plateau at an approximate concentration of 2 mg/l when the carbon masses are over 400 mg; 2) over-estimation of the carbon masses did not allow to differentiate between the adsorptive capacity of GAC for o-cresol under oxic and aerobic conditions. This is noticed more clearly in figure 4.13 that shows the liquid phase

Table 4.12: Adsorption Model Constants of Langmuir Equation for o-Cresol

Isotherm Type	Q	b	R ²	SSE
oxygen purged	296.5	.1334	.996	.022
non purging	312.9	.0717	.991	.04
nitrogen purged	213.4	.0259	.986	.17

Table 4.13: Adsorption Model Constants of Freundlich Equation for o-Cresol

Isotherm Type	K	1/n	R ²	SSE
oxygen purged	147.1	.114	.89	.0159
non purging	121.3	.15	.861	.0412
nitrogen purged	58.1	.197	.972	.0035

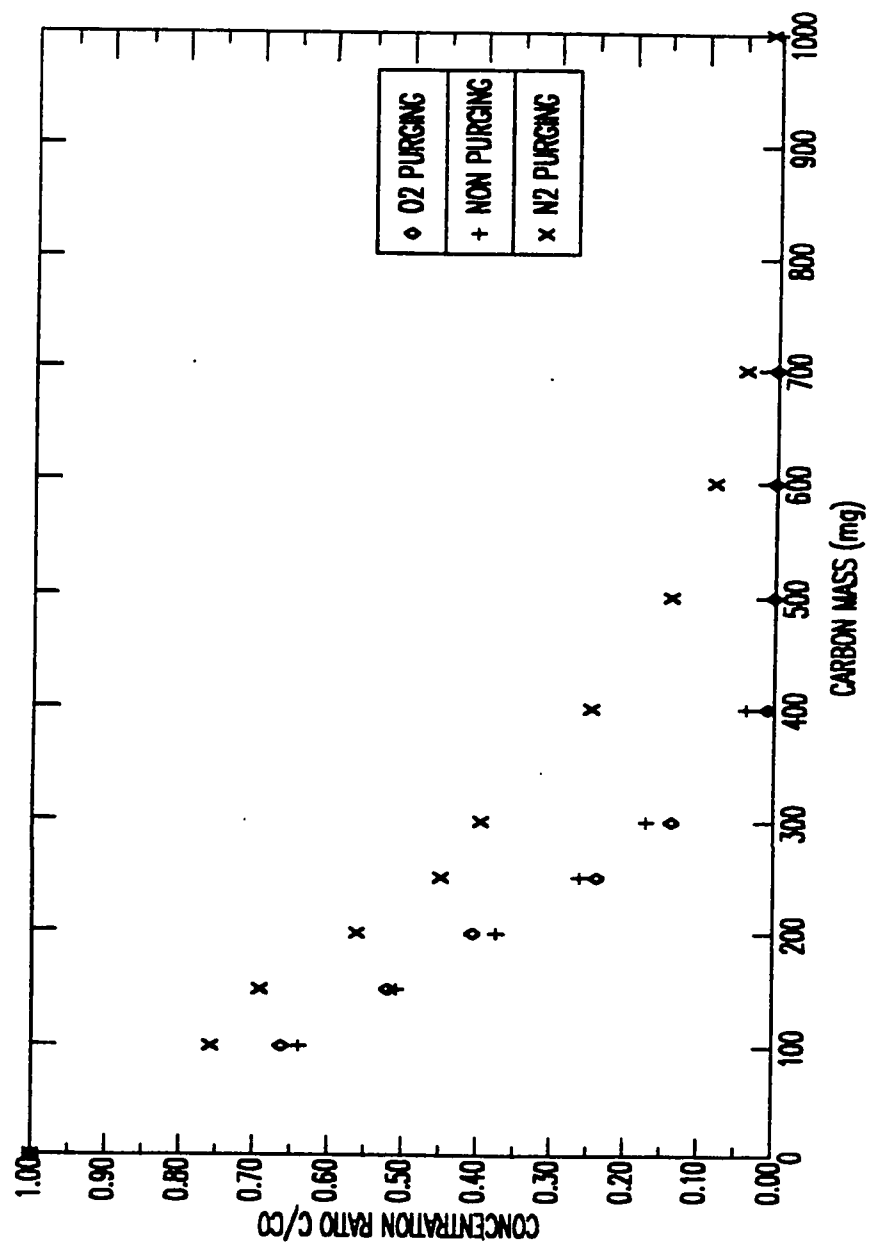


Figure 4.13: Relationship between Residual o-Cresol Concentration and Carbon Dosage

concentration over the initial phase concentration ratio plotted as a function of carbon mass. The ratio approaches zero when the carbon masses are over 400 mg under oxic and aerobic conditions.

However, figures 4.10 to 4.12 indicate higher adsorptive capacity of GAC in oxic and aerobic conditions than anoxic conditions. For low concentrations, for example at 1 mg/l of liquid phase concentration of o-cresol, the adsorptive capacity of GAC under oxic conditions is 141.4% higher than anoxic conditions and 3.7% higher than aerobic conditions, while the adsorptive capacity of GAC under aerobic conditions is 133% higher than anoxic conditions. For high concentrations, for example at 1000 mg/l of liquid phase concentration of o-cresol, the adsorptive capacity of GAC under oxic and aerobic conditions is 50% higher than anoxic conditions.

To corroborate these findings, and to eliminate the experimental error factor, statistical analysis was carried out using SAS program. The null-hypothesis that attributes the differences in adsorptive capacities of GAC due to the dominance of oxygen to random errors was tested. The analysis of variance presented in Appendix 6 clearly show that the null-hypothesis is strictly rejected at α value as low as 0.0001.

4.3 Practical implementation

As the experimental results indicate, a new method for regeneration of carbon is introduced, that is, a simple mechanical

aeration process. This method is cheaper than the non-regeneration methods used that provide thermal treatment of the carbon to about 960°C or exchanging the exhausted carbon. This is true if the exhaustion is reversible.

In practice, in the industrial treatment plants using GAC for treatment, it is suggested to oxygenate the industrial wastewater before adding the carbon masses. The oxygen must be purged before the carbon masses are added as one trial bottle was prepared with the addition of GAC before oxygen purging, and the results showed lower adsorptive capacity of GAC.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This study is an experimental evaluation of the effect of molecular oxygen on the adsorptive capacity of granular activated charcoal (GAC) at bench scale.

Batch single solute adsorption isotherms experiments were conducted on phenol and o-cresol adsorbate because of their common presence in effluents from many petroleum and petrochemical industries. The procedure used is the standard static point procedure with modifications that a new procedure for obtaining adsorption equilibrium data is introduced in this study. This procedure, denoted as oxic, differs from the currently used method, denoted as aerobic. It recommends the inclusion or saturation of molecular oxygen in the adsorption process. A third procedure is used denoted as anoxic, which includes exclusion or elimination of the molecular oxygen in the adsorption process, and it was described by Vidic et. al. [35]. The equilibration period used for phenol and o-cresol isotherms was ten days at neutral pH and room temperature (23°C).

The phenol and o-cresol isotherms were better described by the Freundlich model in terms of the sum of the squared errors (SSE). All the calculations needed for determining the constants in this study were done by the SAS program.

The GAC adsorptive capacity for phenol and o-cresol used in this study increases in the presence of molecular oxygen. Not only the presence of oxygen but also the amount of the molecular oxygen has an effect on the adsorptive capacity of GAC. For phenol, at the equilibrium concentration of 1000 mg/l, for example, the adsorptive capacity of GAC exhibited under oxic conditions 41% higher than anoxic adsorptive capacity, and 4.3% higher than the aerobic adsorptive capacity. While the aerobic adsorptive capacity is 35% higher than the anoxic adsorptive capacity. These differences in GAC adsorptive capacity are more noticed in the lower concentration. For the equilibrium concentration of 1 mg/l, for example, the oxic GAC adsorptive capacity is 167% higher than the anoxic adsorptive capacity, and 60% higher than the aerobic adsorptive capacity, while the aerobic adsorptive capacity is 67% higher than the anoxic adsorptive capacity. Likewise for o-cresol at low concentrations, for example at 1 mg/l of liquid phase concentration, the adsorptive capacity of GAC under oxic conditions is 141.4% higher than anoxic conditions and 3.7% higher than aerobic conditions, while the adsorptive capacity of GAC under aerobic conditions is 133% higher than anoxic conditions. For high concentrations, for example at 1000 mg/l of liquid phase concentration, the adsorptive capacity of GAC

under oxic and aerobic conditions is 50% higher than anoxic conditions. Statistical analysis of the discrepancies between the corresponding residual concentrations and the adsorbed quantities of phenol and o-cresol at identical carbon masses under different conditions revealed and emphasized the reality of this finding. It was proven experimentally that biological degradation was not responsible for the higher observed adsorptive capacities under oxic and aerobic conditions.

This finding introduces a new and cheap process for the regeneration of reversible exhausted carbon by increasing its capacity by simple mechanical aeration. However, further research is needed to get more insight on the effect of molecular oxygen on the adsorptive capacity of carbon with other parameters such as, temperature, pH, equilibration period, and for more compounds and/in other organic groups.

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APPENDIX I

SAS Listings for Phenol Isotherms Modelled by Langmuir Equation

12:25 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	511	2.9900
2	429	3.2260
3	382	3.3400
4	180	1.8182
5	101	1.0980
6	58	0.6720
7	39	0.4815

REGRESSION ANALYSIS

12:25 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	8.37073167	8.37073167	52.05	0.0008	0.912357	20.6021
ERROR	5	0.80411147	0.16082229				Q MEAN
CORRECTED TOTAL	6	9.17484313					1.94652857

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	8.37073167	52.05	0.0008	1	8.37073167	52.05	0.0008

STD ERROR OF ESTIMATE

PR > |T|

T FOR H0:
PARAMETER=00.25494645
0.000844100.1261
0.00081.83
7.210.46758189
0.00608978

PARAMETER

INTERCEPT

UPPER 95% CL
FOR MEANLOWER 95% CL
FOR MEAN

RESIDUAL

PREDICTED
VALUEOBSERVED
VALUE4.27968629
3.64129070
3.28678741
1.97655073
1.57918825
1.37997772
1.294543352.87923312
2.51890472
2.30096864
1.15093401
0.58611117
0.26160058
0.11562330-0.58945971
0.14590229
0.54612197
0.25445763
0.01535029
-0.14878915
-0.223583323.57945971
3.08009771
2.79387803
1.56374237
1.08264971
0.82078915
0.705083322.99000000
3.22600000
3.34000000
1.81820000
1.09800000
0.67200000
0.481500000.00000000
0.80411147
-0.00000000
1.98908926
0.20834256
1.08903981SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

1	VARIABLE	N	MEAN	STD DEV	RECESSION ANALYSIS	SUM	12:25 THURSDAY, DECEMBER 27, 1990	3
	Q	7	1.94652857	1.23658422		13.62570000	MINIMUM	MAXIMUM
	C	7	242.85714286	193.95654889		1700.00000000	0.48150000	3.34000000
							39.00000000	511.00000000

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 7

	Q	C
Q	1.00000 0.95517	0.0000 0.0008
C	0.95517 1.00000	0.0008 0.0000

12:29 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	453.0	2.3230
2	290.0	1.6960
3	64.0	0.5600
4	15.0	0.1470
5	11.6	0.1275
6	8.6	0.1024
7	3.4	0.0500

12:29 THURSDAY, DECEMBER 27, 1990 2

REGRESSION ANALYSIS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	5.01008340	5.01008340	530.16	0.0001	0.990657	13.5936
ERROR	5	0.04725050	0.00945010				Q MEAN
CORRECTED TOTAL	6	5.05733389			0.09721162		0.71512857

SOURCE	DF	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	530.16	0.0001	1	5.01008340	530.16	0.0001

STD ERROR OF ESTIMATE

PR > |T|

T FOR H0:
PARAMETER=0

INTERCEPT	0.09757229	2.14
C	0.00511222	23.03

0.0848
0.0001

OBSERVATION	ESTIMATE	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.32300000	2.32300000	2.41340834	-0.09040834	2.20158936	2.62522733
2	1.69600000	1.69600000	1.58011634	0.11588366	1.44503947	1.71519322
3	0.56000000	0.56000000	0.42675443	0.13524557	0.32489764	0.52461122
4	0.14700000	0.14700000	0.17425560	-0.02725560	0.06215467	0.28635653
5	0.12750000	0.12750000	0.15687405	-0.02937405	0.04371607	0.27003203
6	0.10240000	0.10240000	0.14153739	-0.03913739	0.02742744	0.25564734
7	0.05000000	0.05000000	0.11495384	-0.06495384	-0.00084762	0.23075530

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

0.00000000
0.04725050
-0.00000000
0.16769388
0.12702634
1.48367134

VARIABLE	N	REGRESSION ANALYSIS			12:29 THURSDAY, DECEMBER 27, 1990		3
		MEAN	STD DEV	SUM	MINIMUM	MAXIMUM	
Q	7	0.71512857	0.91808986	5.00590000	0.05000000	2.32300000	
C	7	120.80000000	178.74637525	845.60000000	3.40000000	453.00000000	

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0: RHO=0 / N = 7

	Q	C
Q	1.00000	0.99532
	0.0000	0.0001
C	0.99532	1.00000
	0.0001	0.0000

12:34 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	435.0	2.14600
2	205.0	1.05700
3	134.0	0.81710
4	27.3	0.18320
5	6.3	0.05164
6	3.8	0.03690
7	1.1	0.01300

REGRESSION ANALYSIS

12:34 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	3.76360645	3.76360645	1107.45	0.0001	0.995505	9.4794
ERROR	5	0.01699229	0.00339846				Q MEAN
CORRECTED TOTAL	6	3.78059875					0.61497714
						0.05829630	

ROOT MSE

0.05829630

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	3.76360645	1107.45	0.0001	1	3.76360645	1107.45	0.0001

STD ERROR OF ESTIMATE

PR > |T|

T FOR HO: PARAMETER=0

PARAMETER	ESTIMATE
INTERCEPT	0.04430709
C	0.00491654

1.59
33.280.02792064
0.00014774

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.14600000	2.18300287	-0.03700287	2.04929369	2.31671205
2	1.05700000	1.05219820	0.00480180	0.98625436	1.11814205
3	0.81710000	0.70312372	0.11397628	0.64607673	0.76017070
4	0.18320000	0.17852868	0.00467132	0.11261538	0.24444198
5	0.05164000	0.07528130	-0.02364130	0.00495418	0.14560842
6	0.03690000	0.06298995	-0.02608995	-0.00790410	0.13388399
7	0.01300000	0.04971528	-0.03671528	-0.02180015	0.12123072

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

0.00000000
0.01699229
0.00000000
0.05509235
0.13925691
1.56157696

1	VARIABLE	N	REGRESSION ANALYSIS				12:34 THURSDAY, DECEMBER 27, 1990		3
			MEAN	STD DEV	SUM		MINIMUM	MAXIMUM	
	Q	7	0.61497714	0.79378825	4.30484000		0.01300000	2.14600000	
	C	7	116.07142857	161.08930975	812.50000000		1.10000000	435.00000000	

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0: RHO=0 / N = 7

	Q	C
Q	1.00000 0.99775 0.0000 0.0001	
C	0.99775 1.00000 0.0001 0.0000	

APPENDIX II

SAS Listings for Phenol Isotherms Modelled by Freundlich Equation

1 REGRESSION ANALYSIS 11:51 THURSDAY, DECEMBER 27, 1990 1

OBS	C	Q
1	2.70842	2.23300
2	2.63246	2.12385
3	2.58206	2.05077
4	2.25527	1.99564
5	2.00432	1.96379
6	1.76343	1.93601
7	1.59106	1.90849

1 REGRESSION ANALYSIS 11:51 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.06475920	0.06475920	21.80	0.0055	0.813442	2.6845
ERROR	5	0.01485211	0.00297042				Q MEAN
CORRECTED TOTAL	6	0.07961131					2.03021899

SOURCE	DF	TYPE I SS	F VALUE	PR > F	STD ERROR OF ESTIMATE	TYPE III SS	F VALUE	PR > F
C	1	0.06475920	21.80	0.0055	0.11271979	0.06475920	21.80	0.0055

PARAMETER ESTIMATE T FOR H0: PARAMETER=0 PR > |T|

INTERCEPT	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
C	1.51277227	13.42	0.0001	0.11271979
	0.23312869	4.67	0.0055	0.04992914

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.23299611	2.14418289	0.08881322	2.06208311	2.22628267
2	2.12385164	2.12647359	-0.00262195	2.05156008	2.20138711
3	2.05076631	2.11472532	-0.06395901	2.04423851	2.18521214
4	1.99563519	2.03854100	-0.04290580	1.98539082	2.09169118
5	1.96378783	1.98003709	-0.01624926	1.92031112	2.03976306
6	1.93601080	1.92387793	0.01213287	1.84493881	2.00281705
7	1.90848502	1.88369508	0.02478994	1.78720156	1.98018860

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

1	VARIABLE	N	REGRESSION ANALYSIS				11:51 THURSDAY, DECEMBER 27, 1990	3
			MEAN	STD DEV	SUM	MINIMUM		
Q		7	2.03021899	0.11518920	14.21153290	1.90848502		
C		7	2.21957543	0.44563508	15.53702803	1.59106461		
								MAXIMUM
								2.23299611
								2.70842090

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 7

	Q	C
Q	1.00000	0.90191
	0.0000	0.0055
C	0.90191	1.00000
	0.0055	0.0000

1 11:54 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	2.65610	2.29003
2	2.46240	2.23300
3	1.80618	2.05805
4	1.17609	2.00860
5	1.06446	1.95904
6	0.93450	1.92428
7	0.53148	1.83251

1 11:54 THURSDAY, DECEMBER 27, 1990 2

REGRESSION ANALYSIS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.16044054	0.16044054	226.54	0.0001	0.978406	1.3022
ERROR	5	0.00354107	0.00070821				Q MEAN
CORRECTED TOTAL	6	0.16398161					2.04364382
					0.02661230		
					ROOT MSE		

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	0.16044054	226.54	0.0001	1	0.16044054	226.54	0.0001

PARAMETER	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
INTERCEPT	1.73585873	76.17	0.0001	0.02278896
C	0.20265775	15.05	0.0001	0.01346445

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.29003461	2.27413761	0.01589700	2.22704065	2.32123456
2	2.23299611	2.23488276	-0.00188665	2.19322641	2.27653911
3	2.05804623	2.10189509	-0.04384886	2.07419138	2.12959881
4	2.00860017	1.97420273	0.03439744	1.94575679	2.00264868
5	1.95904139	1.95157939	0.00746200	1.92131812	1.98184066
6	1.92427929	1.92524208	-0.00096279	1.89241795	1.95806622
7	1.83250891	1.84356705	-0.01105814	1.80071703	1.88641707

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.00354107
 0.00000000
 0.00582192
 -0.33758622
 2.56927311

1	VARIABLE	N	REGRESSION ANALYSIS				11:54 THURSDAY, DECEMBER 27, 1990	3
			MEAN	STD DEV	SUM	MINIMUM		
Q		7	2.04364382	0.16531869	14.30550672	1.83250891		
C		7	1.51874326	0.80689722	10.63120279	0.53147892		
								2.29003461
								2.65609820

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 7

	Q	C
Q	1.00000	0.98914
	0.0000	0.0001
C	0.98914	1.00000
	0.0001	0.0000

11:57 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	2.63849	2.30685
2	2.31175	2.28780
3	2.12710	2.21484
4	1.43616	2.17319
5	0.79934	2.08636
6	0.57978	2.01284
7	0.04139	1.92686

REGRESSION ANALYSIS

11:57 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.11722698	0.11722698	166.46	0.0001	0.970839	1.2377
ERROR	5	0.00352119	0.00070424				Q MEAN
CORRECTED TOTAL	6	0.12074816					2.14410562
							0.02653747

SOURCE	DF	TYPE I SS	F VALUE	PR > F	STD ERROR OF ESTIMATE	TYPE III SS	F VALUE	PR > F
C	1	0.11722698	166.46	0.0001	0.01861000	0.11722698	166.46	0.0001

PR > |T|

T FOR HQ:
PARAMETER=0

PARAMETER	ESTIMATE
INTERCEPT	1.94185941
C	0.14251254

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.30685375	2.31787722	-0.01102347	2.27470965	2.36104480
2	2.28780173	2.27131333	0.01648840	2.23515928	2.30746738
3	2.21484385	2.24499852	-0.03015467	2.21230531	2.27769173
4	2.17318627	2.14653060	0.02665567	2.12078294	2.17231826
5	2.08635983	2.05577546	0.03058437	2.02455875	2.08699218
6	2.01283722	2.02448584	-0.01164862	1.98937503	2.05959666
7	1.92685671	1.94775838	-0.02090167	1.90090625	1.99461051

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

0.00000000
0.00352119
0.00000000
0.00667660
-0.22160081
2.28461963

VARIABLE	N	REGRESSION ANALYSIS			11:57 THURSDAY, DECEMBER 27, 1990		3
		MEAN	STD DEV	SUM	MINIMUM	MAXIMUM	
Q	7	2.14410562	0.14186153	15.00873936	1.92685671	2.30685375	
C	7	1.41914677	0.98081040	9.93402739	0.04139269	2.63848926	

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0: RHO=0 / N = 7

	Q	C
Q	1.00000 0.98531	0.00000 0.0001
C	0.98531 1.00000	0.0001 0.0000

APPENDIX III

SAS Listings of ANOVA Table for Phenol

1SAS

8:54 SATURDAY, DECEMBER 29, 1990 1

GENERAL LINEAR MODELS PROCEDURE

CLASS LEVEL INFORMATION

CLASS LEVELS VALUES

TREAT 3 1 2 3

BLOCKS 8 1 2 3 4 5 6 7 8

NUMBER OF OBSERVATIONS IN DATA SET = 24

NOTE: ALL DEPENDENT VARIABLES ARE CONSISTENT WITH RESPECT TO THE PRESENCE OR ABSENCE OF MISSING VALUES. HOWEVER,
ONLY 20 OBSERVATIONS CAN BE USED IN THIS ANALYSIS.

1SAS

8:54 SATURDAY, DECEMBER 29, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YIELD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	9	31538.37583217	3504.26398135	25.16	0.0001	0.957699	9.2526
ERROR	10	1393.03216783	139.30321678		ROOT MSE	YIELD MEAN	
CORRECTED TOTAL	19	32931.40800000			11.60267837	127.56000000	

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
TREAT	2	4285.48538095	15.38	0.0009	2	2749.31283217	9.87	0.0043
BLOCKS	7	27252.89045122	27.95	0.0001	7	27252.89045122	27.95	0.0001

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	171.00000000	173.92820513	-2.92820513	156.56548708	191.29092317
2	133.00000000	150.36153846	-17.36153846	132.99882041	167.72425651
3	112.00000000	123.59160839	-11.59160839	103.55627456	143.62694222
4 *		119.78321678		89.54971591	150.01671765
5	99.00000000	96.12820513	2.87179487	78.76548708	113.49092317
6	92.00000000	83.36153846	8.63846154	65.99882041	100.72425651
7	86.30000000	79.80069930	6.49930070	59.76536547	99.83603313
8	81.00000000	67.52820513	13.47179487	50.16548708	84.89092317
9	195.00000000	191.62680653	3.37319347	173.98774139	209.26587167
10	171.00000000	168.06013986	2.93986014	150.42107472	185.69920500
11 *		141.29020979		118.33026783	164.25015175
12 *		137.48181818		106.77216989	168.19146647
13	114.30000000	113.82680653	0.47319347	96.18774139	131.46587167

14	102.00000000	101.06013986	0.93986014	83.42107472	118.69920500
15	91.00000000	97.99930070	-6.49930070	77.46396687	117.53463453
16	84.00000000	85.22680653	-1.22680653	67.58774139	102.86587167
17	202.70000000	203.14498834	-0.44498834	185.50592321	220.78405348
18	194.00000000	179.57832168	14.42167832	161.93925654	197.21738682
19	164.00000000	152.80839161	11.19160839	132.77305778	172.84372544
20	149.00000000	149.00000000	0.00000000	122.70182836	175.29817164
21	122.00000000	125.34498834	-3.34498834	107.70592321	142.98405348
22	103.00000000	112.57832168	-9.57832168	94.93925654	130.21738682
23 *	.	109.01748252	.	86.05754056	131.97742448
24	84.50000000	96.74498834	-12.24498834	79.10592321	114.38405348

* OBSERVATION WAS NOT USED IN THIS ANALYSIS

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 1393.03216783
 0.00000000
 10881.17216934
 0.53511133
 0.81596663

1RANDOMIZE BLOCK DESIGN

ADSORPTION ISOTHERM

OBS TREAT BLOCKS YIELD

1	1	1	171.0
2	1	2	133.0
3	1	3	112.4
4	1	4	.
5	1	5	99.0
6	1	6	92.0
7	1	7	86.3
8	1	8	81.0
9	2	1	195.0
10	2	2	171.0
11	2	3	.
12	2	4	.
13	2	5	114.3
14	2	6	102.0
15	2	7	91.0
16	2	8	84.0
17	3	1	202.7
18	3	2	194.0
19	3	3	164.0
20	3	4	149.0
21	3	5	122.0
22	3	6	103.0
23	3	7	.
24	3	8	84.5

APPENDIX IV

SAS Listings for o-Cresol Isotherms Modelled by Langmuir Equation

12:39 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	686	3.118
2	626	3.353
3	509	2.564
4	408	2.048
5	359	1.969
6	225	1.321
7	127	0.815
8	75	0.542
9	40	0.323
10	11	0.123

12:39 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	12.09591098	12.09591098	568.64	0.0001	0.986127	9.0163
ERROR	8	0.17017342	0.02127168			ROOT MSE	Q MEAN
CORRECTED TOTAL	9	12.26608440				0.14584813	1.61760000
SOURCE	DF	TYPE I SS		DF	TYPE III SS	F VALUE	PR > F
C	1	12.09591098	568.64	1	12.09591098	568.64	0.0001

STD ERROR OF ESTIMATE

PR > |T|

T FOR HO:
PARAMETER=0

PARAMETER ESTIMATE

0.07567146
0.000196490.0441
0.0001INTERCEPT
0.18101787
0.00468553

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	3.11800000	3.39528839	-0.27728839	3.19313781	3.59743898
2	3.35300000	3.11415686	0.23884314	2.93455548	3.29375824
3	2.56400000	2.56595037	-0.00195037	2.42551388	2.70638686
4	2.04800000	2.09271229	-0.04471229	1.97685573	2.20856885
5	1.96900000	1.86312154	0.10587846	1.75414680	1.97209627
6	1.32100000	1.23526112	0.08573888	1.12266082	1.34786141
7	0.81500000	0.77607961	0.03892039	0.64216080	0.90999842
8	0.54200000	0.53243228	0.00956772	0.38301926	0.68184530
9	0.32300000	0.36843889	-0.04543889	0.20749099	0.52938679
10	0.12300000	0.23255865	-0.10955865	0.06152781	0.40358948

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.17017342
 -0.00000000
 0.35358439
 -0.31738433
 2.11240772

REGRESSION ANALYSIS

12:39 THURSDAY, DECEMBER 27, 1990 3

VARIABLE	N	MEAN	STD DEV	SUM	MINIMUM	MAXIMUM
Q	10	1.61760000	1.16743234	16.17600000	0.12300000	3.35300000
C	10	306.60000000	247.42280502	3066.00000000	11.00000000	686.00000000

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 10

	Q	C
--	---	---

Q	1.00000	0.99304
	0.0000	0.0001

C	0.99304	1.00000
	0.0001	0.0000

12:43 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	579.00	1.7710
2	461.00	1.5540
3	339.00	1.1960
4	237.00	0.8860
5	155.00	0.6190
6	34.00	0.1560
7	2.50	0.0138
8	1.94	0.0129
9	1.60	0.0124
10	1.55	0.0171

12:43 THURSDAY, DECEMBER 27, 1990 2

REGRESSION ANALYSIS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	4.24355560	4.24355560	848.72	0.0001	0.990662	11.3350
ERROR	8	0.03999950	0.00499994				Q MEAN
CORRECTED TOTAL	9	4.28355510					0.62382000

SOURCE	DF	TYPE I SS	F VALUE	PR > F	STD ERROR OF ESTIMATE	TYPE III SS	F VALUE	PR > F
C	1	4.24355560	848.72	0.0001	0.02992247	4.24355560	848.72	0.0001

PARAMETER ESTIMATE

PARAMETER	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
INTERCEPT	0.04455251	1.49	0.1748	0.02992247
C	0.00319580	29.13	0.0001	0.00010970

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	1.77100000	1.89492064	-0.12392064	1.78186239	2.00797890
2	1.55400000	1.51781626	0.03618374	1.43025769	1.60537483
3	1.19600000	1.12792867	0.06807133	1.06272824	1.19312910
4	0.88600000	0.80195708	0.08404292	0.74849989	0.85541427
5	0.61900000	0.53990149	0.07909851	0.48791140	0.59189159
6	0.15600000	0.15320970	0.00279030	0.08959748	0.21682193
7	0.01380000	0.05254201	-0.03874201	-0.01604137	0.12112539
8	0.01290000	0.05075236	-0.03785236	-0.01792451	0.11942923
9	0.01240000	0.04966579	-0.03726579	-0.01906792	0.11839949
10	0.01710000	0.04950600	-0.03240600	-0.01923607	0.11824807

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.03999950
 -0.00000000
 0.09067383
 0.36363109
 0.86257082

REGRESSION ANALYSIS

VARIABLE	N	MEAN	STD DEV	SUM	MINIMUM	MAXIMUM
Q	10	0.62382000	0.68989171	6.23820000	0.01240000	1.77100000
C	10	181.25900000	214.86422723	1812.59000000	1.55000000	579.00000000

12:43 THURSDAY, DECEMBER 27, 1990 3

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 10

Q C

Q 1.00000 0.99532
 0.0000 0.0001

C 0.99532 1.00000
 0.0001 0.0000

12:46 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	600.00	1.96080
2	471.00	1.62400
3	368.00	1.36800
4	217.00	0.78740
5	124.00	0.47560
6	8.70	0.03880
7	2.30	0.01273
8	1.94	0.01287
9	1.55	0.01200
10	1.55	0.01710

REGRESSION ANALYSIS

12:46 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C. V.	
MODEL	1	5.19960323	5.19960323	1919.52	0.0001	0.995850	8.2491	
ERROR	8	0.02167042	0.00270880		ROOT MSE		Q MEAN	
CORRECTED TOTAL	9	5.22127365			0.05204616		0.63093000	
SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	5.19960323	1919.52	0.0001	1	5.19960323	1919.52	0.0001

T FOR H0: PARAMETER=0

PARAMETER	ESTIMATE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
INTERCEPT	0.02527222	1.18	-0.08778276	1.96486795	2.13229758
C	0.00337218	43.81	0.01042900	1.54941895	1.67772305

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	1.96080000	2.04858276	-0.08778276	1.96486795	2.13229758
2	1.62400000	1.61337100	0.01042900	1.54941895	1.67772305
3	1.36800000	1.26623602	0.10176398	1.21565312	1.31681892
4	0.78740000	0.75703620	0.03036380	0.71850658	0.79556583
5	0.47560000	0.44342307	0.03217693	0.40420728	0.48263886
6	0.03880000	0.05461023	-0.01581023	0.00602387	0.10319658
7	0.01273000	0.03302825	-0.02029825	-0.01627531	0.08233180
8	0.01287000	0.03181426	-0.01894426	-0.01753011	0.08115863
9	0.01200000	0.03049911	-0.01849911	-0.01888952	0.07988774
10	0.01710000	0.03049911	-0.01339911	-0.01888952	0.07988774

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.02167042
 -0.00000000
 0.04942498
 0.23109007
 1.17394369

REGRESSION ANALYSIS

12:46 THURSDAY, DECEMBER 27, 1990 3

VARIABLE	N	MEAN	STD DEV	SUM	MINIMUM	MAXIMUM
Q	10	0.63093000	0.76167022	6.30930000	0.01200000	1.96080000
C	10	179.60400000	225.39929519	1796.04000000	1.55000000	600.00000000

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0: RHO=0 / N = 10

Q C

Q	1.00000	0.99792
	0.0000	0.0001
C	0.99792	1.00000
	0.0001	0.0000

APPENDIX V

SAS Listings for o-Cresol Isotherms Modelled by Freundlich Equation

11:08 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	2.83632	2.34242
2	2.79657	2.27114
3	2.70672	2.29776
4	2.61066	2.29929
5	2.55509	2.26079
6	2.35218	2.23121
7	2.10380	2.19257
8	1.87506	2.14145
9	1.60206	2.09237
10	1.04139	1.95182

11:08 THURSDAY, DECEMBER 27, 1990 2

REGRESSION ANALYSIS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.12192266	0.12192266	277.56	0.0001	0.971985	0.9492
ERROR	8	0.00351408	0.00043926				Q MEAN
CORRECTED TOTAL	9	0.12543674			0.02095852		2.20808281

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	0.12192266	277.56	0.0001	1	0.12192266	277.56	0.0001

PARAMETER	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
-----------	----------	--------------------------	---------	--------------------------

INTERCEPT	1.76420893	64.26	0.0001	0.02745466
C	0.19745393	16.66	0.0001	0.01185179

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.34242268	2.32425227	0.01817041	2.30206803	2.34643650
2	2.27114432	2.31640352	-0.04525920	2.29499363	2.33781340
3	2.29776051	2.29866099	-0.00090048	2.27889301	2.31842896
4	2.29928933	2.27959403	0.01959530	2.26147766	2.29791041
5	2.26078667	2.26872236	-0.00793570	2.25128571	2.28615902
6	2.23121465	2.22865661	0.00255804	2.21311000	2.24420321
7	2.19256745	2.17961324	0.01295422	2.16382983	2.19539664
8	2.14144977	2.13444714	0.00700263	2.11607679	2.15281749
9	2.09236970	2.08054197	0.01182773	2.05719170	2.10389224
10	1.95182304	1.96983601	-0.01801297	1.93348958	2.00618243

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.00351408
 -0.00000000
 0.00654928
 -0.27929029
 2.37229230

REGRESSION ANALYSIS

11:08 THURSDAY, DECEMBER 27, 1990 3

VARIABLE	N	MEAN	STD DEV	SUM	MINIMUM	MAXIMUM
Q	10	2.20808281	0.11805683	22.08082812	1.95182304	2.34242268
C	10	2.24798710	0.58946115	22.47987102	1.04139269	2.83632412

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0: RHO=0 / N = 10

	Q	C
Q	1.00000	0.98589
	0.0000	0.0001
C	0.98589	1.00000
	0.0001	0.0000

1

REGRESSION ANALYSIS

11:16 THURSDAY, DECEMBER 27, 1990 1

OBS	C	Q
1	2.76268	2.51455
2	2.66370	2.47232
3	2.53020	2.45255
4	2.37475	2.42749
5	2.19033	2.39846
6	1.53148	2.33846
7	0.39794	2.25696
8	0.28780	2.17811
9	0.20412	2.11126
10	0.19033	1.95665

1

REGRESSION ANALYSIS

11:16 THURSDAY, DECEMBER 27, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.25428357	0.25428357	49.35	0.0001	0.860511	3.1065
ERROR	8	0.04121939	0.00515242				Q MEAN
CORRECTED TOTAL	9	0.29550296					2.31068043

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	0.25428357	49.35	0.0001	1	0.25428357	49.35	0.0001

PARAMETER	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
INTERCEPT	2.08395943	52.82	0.0001	0.03945611
C	0.14981566	7.03	0.0001	0.02132573

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.51454775	2.49785194	0.01669582	2.41713764	2.57856623
2	2.47231755	2.48302354	-0.01070599	2.40594972	2.56009736
3	2.45255306	2.46302296	-0.01046990	2.39063064	2.53541529
4	2.42748611	2.43973392	-0.01224781	2.37239516	2.50707267
5	2.39846085	2.41210541	-0.01364456	2.35007016	2.47414067
6	2.33845649	2.31339895	0.02505754	2.26104697	2.36575094
7	2.25695815	2.14357707	0.11338108	2.06775672	2.21939742
8	2.17811325	2.12707663	0.05103662	2.04725018	2.20690309
9	2.1126251	2.11453980	-0.00237228	2.03156243	2.19751716
10	1.95664858	2.11247410	-0.15582552	2.02896950	2.19597869

SUM OF RESIDUALS
 SUM OF SQUARED RESIDUALS
 SUM OF SQUARED RESIDUALS - ERROR SS
 PRESS STATISTIC
 FIRST ORDER AUTOCORRELATION
 DURBIN-WATSON D

0.00000000
 0.04121939
 -0.00000000
 0.07079651
 0.21489539
 0.97436482

1	VARIABLE	N	MEAN	STD DEV	SUM	11:16 THURSDAY, DECEMBER 27, 1990		3
						MINIMUM	MAXIMUM	
Q		10	2.31068043	0.18120061	23.10680431	1.95664858	2.51454775	
C		10	1.51333316	1.12196856	15.13333157	0.19033170	2.76267856	

REGRESSION ANALYSIS

PEARSON CORRELATION COEFFICIENTS / PROB > |RI| UNDER H0:RHO=0 / N = 10

	Q	C
Q	1.00000	0.92764
	0.0000	0.0001
C	0.92764	1.00000
	0.0001	0.0000

11:42 THURSDAY, DECEMBER 27, 1990 1

REGRESSION ANALYSIS

OBS	C	Q
1	2.77815	2.48572
2	2.67302	2.46240
3	2.56585	2.42975
4	2.33646	2.44028
5	2.09342	2.41614
6	0.93952	2.35083
7	0.36173	2.25696
8	0.28780	2.17811
9	0.19033	2.11126

11:42 THURSDAY, DECEMBER 27, 1990 2

REGRESSION ANALYSIS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: Q

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	1	0.12924226	0.12924226	57.05	0.0001	0.890718	2.0271
ERROR	7	0.01585665	0.00226524			ROOT MSE	Q MEAN
CORRECTED TOTAL	8	0.14509892				0.04759450	2.34793946

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
C	1	0.12924226	57.05	0.0001	1	0.12924226	57.05	0.0001

PARAMETER	ESTIMATE	T FOR H0: PARAMETER=0	PR > T	STD ERROR OF ESTIMATE
INTERCEPT	2.16763625	75.63	0.0001	0.02866155
C	0.11406557	7.55	0.0001	0.01510112

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	2.48572143	2.48452764	0.00119378	2.42764416	2.54141113
2	2.46239800	2.47233589	-0.01013789	2.41841770	2.52665408
3	2.42975228	2.46031113	-0.03055885	2.40888278	2.51173949
4	2.44027921	2.43414585	0.00613336	2.38793259	2.48035911
5	2.41614103	2.40642358	0.00971745	2.36467960	2.44816756
6	2.35082927	2.27480304	0.07602623	2.23085349	2.31875260
7	2.25695815	2.20889694	0.04806121	2.15143366	2.26636022
8	2.17811325	2.20046452	-0.02235126	2.14097663	2.25995240
9	2.11126251	2.18934654	-0.07808403	2.12711874	2.25157434

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS

0.00000000
0.01585665

SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

-0.00000000
0.02773408
0.33005790
0.95227973

1	VARIABLE	N	MEAN	STD DEV	SUM	11:42 THURSDAY, DECEMBER 27, 1990	
						MINIMUM	MAXIMUM
Q	C	9	2.34793946	0.13467503	21.13145514	2.11126251	2.48572143
		9	1.58069799	1.11430151	14.22628191	0.19033170	2.77815125

REPRESSION ANALYSIS

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 9

Q	C	Q	C
1.00000	0.94378	0.0000	0.0001
0.0000	0.0001	0.94378	1.00000
		0.0001	0.0000

APPENDIX VI

SAS Listings of ANOVA Table for o-Cresol

1SAS

8:44 SATURDAY, DECEMBER 29, 1990 1

GENERAL LINEAR MODELS PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
TREAT	3	1 2 3
BLOCKS	10	1 2 3 4 5 6 7 8 9 10

NUMBER OF OBSERVATIONS IN DATA SET = 30
1SAS

8:44 SATURDAY, DECEMBER 29, 1990 2

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YIELD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	11	129585.20122676	11780.47283880	22.34	0.0001	0.931757	11.4139
ERROR	18	9490.97609348	527.27644964				YIELD MEAN
CORRECTED TOTAL	29	139076.17732024					201.18001667

ROOT MSE

22.96250094

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
TREAT	2	18107.92424002	17.17	0.0001	2	18107.92424002	17.17	0.0001
BLOCKS	9	111477.27698674	23.49	0.0001	9	111477.27698674	23.49	0.0001

OBSERVATION	OBSERVED VALUE	PREDICTED VALUE	RESIDUAL	LOWER 95% CL FOR MEAN	UPPER 95% CL FOR MEAN
1	220.70000000	249.60331667	-29.60331667	219.09233012	280.11430321
2	186.70000000	223.06998333	-36.36998333	192.55899679	253.58098988
3	198.50000000	215.60331667	-17.10331667	185.09233012	246.11430321
4	199.20000000	212.73665000	-13.53665000	182.22566346	243.24763654
5	182.30000000	196.36998333	-14.06998333	165.85899679	226.88096988
6	170.30000000	169.46998333	0.83001667	138.95899679	199.98096988
7	155.80000000	137.66998333	18.13001667	107.15899679	168.18096988
8	138.50000000	111.90331667	26.59668333	81.39233012	142.41430321
9	123.70000000	92.63665000	31.06335000	62.12566346	123.14763654
10	89.50000000	55.43681667	34.06318333	24.92563012	85.94780321
11	327.00000000	302.57336667	24.42663333	272.06238012	333.08435321
12	296.70000000	276.04003333	20.65996667	245.52904679	306.55101988
13	283.50000000	268.57336667	14.92663333	238.06238012	299.08435321
14	267.60000000	265.70670000	1.89330000	235.19571346	296.21768654
15	250.30000000	249.34003333	0.95996667	218.82904679	279.85101988
16	218.00000000	222.44003333	-4.44003333	191.92904679	252.95101988
17	180.70000000	190.64003333	-9.94003333	160.12904679	221.15101988

18	150.70000000	164.87336667	-14.17336667	134.36238012	195.38435321
19	129.20000000	145.60670000	-16.40670000	115.09571346	176.11768654
20	90.50050000	108.40686667	-17.90636667	77.89588012	138.91785321
21	306.00000000	300.82331667	5.17668333	270.31233012	331.33430321
22	290.00000000	274.28998333	15.71001667	243.77899679	304.80096988
23	269.00000000	266.82331667	2.17668333	236.31233012	297.33430321
24	275.60000000	263.95665000	11.64335000	233.44566346	294.46763654
25	260.70000000	247.58998333	13.11001667	217.07899679	278.10096988
26	224.30000000	220.68998333	3.61001667	190.17899679	251.20096988
27	180.70000000	188.88998333	-8.18998333	158.37899679	219.40096988
28	150.70000000	163.12331667	-12.42331667	132.61233012	193.63430321
29	129.20000000	143.85665000	-14.65665000	113.34566346	174.36763654
30	90.50000000	106.65681667	-16.15681667	76.14583012	137.16780321

1SAS

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GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YIELD

SUM OF RESIDUALS
SUM OF SQUARED RESIDUALS
SUM OF SQUARED RESIDUALS - ERROR SS
PRESS STATISTIC
FIRST ORDER AUTOCORRELATION
DURBIN-WATSON D

0.00000000
9490.97609348
-0.00000000
26363.82248190
0.80202732
0.27610530

RANDOMIZE BLOCK DESIGN

ADSORPTION ISOTHERM

OBS TREAT BLOCKS YIELD

1	1	1	220.0
2	1	2	186.7
3	1	3	198.5
4	1	4	199.2
5	1	5	182.3
6	1	6	170.3
7	1	7	155.8
8	1	8	138.5
9	1	9	123.7
10	1	10	89.5
11	2	1	327.0
12	2	2	296.7
13	2	3	283.5
14	2	4	267.6
15	2	5	250.3
16	2	6	218.0
17	2	7	180.7
18	2	8	150.7
19	2	9	129.2
20	2	10	90.5
21	3	1	306.0
22	3	2	290.0
23	3	3	269.0
24	3	4	275.6

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