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REMOVAL OF COLOR AND RESIDUAL CHEMICAL OXYGEN DEMAND FROM SYNFUEL WASTEWATER

Final Technical Report for the Project
April 1, 1987 - March 31, 1988
including the Quarterly Technical Progress Report
for the Period January through March 1988

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NOMENCLATURE

APHA = American Public Health Association
ASTM = American Society for Testing and Materials
ATCC = American Type Culture Collection
BOD = biochemical oxygen demand
CC = Coal Creek
COD = chemical oxygen demand
DIPE = diisopropylether
EMRC = Energy & Mineral Research Center
GS = Gentleman Station
GPGP = Great Plains Gasification Plant
IR = infrared
METC = Morgantown Energy Technology Center
MIBK = methylisobutylketone
MMSCFD = million standard cubic feet per day
MW = megawatts
nm = nanometer
NMR = nuclear magnetic resonance spectrometer
PP = Pleasant Prairie
PtCo = Platinum-cobalt color units
PU = Portage Unit
rpm = revolutions per minute
SGL = stripped gas liquor
SNG = synthetic natural gas
T = transmittance
TOC = total organic carbon
UND = University of North Dakota
UV-Vis = ultraviolet, visible light
YM = Yeast Maintenance

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INTRODUCTION

Color has been classified as a "nonconventional" water pollutant by the Clean Water Act of 1977. This designation allows the government to regulate the amount of color in discharged effluent where warranted. Discharged color detracts from the aesthetic value of the receiving water, and can be a source of public concern. Color may also have negative effects on aquatic life due to decreased light transmittance and toxic effects (Soniassy et al. 1975).

Color removal has been most thoroughly investigated as applicable to the pulp mill industry. Pulp mill effluent is highly colored due to the presence of lignin. Color removal methods include lime coagulation, resin absorption, physical absorption (carbon and flyash), ultrafiltration, reverse osmosis, solvent extraction, and biological (fungi) treatment. Resin absorption, ultrafiltration, and reverse osmosis are relatively expensive for the volume of wastewater treated. Treatment with flyash has been promising (Gupta and Bhattacharya 1984) and is more economical than carbon absorption. An effective method of biological treatment could remove color at one-tenth the cost of physical and chemical treatment.

The production of synthetic natural gas from coal results in a wastewater with high levels of phenols, ammonia, and organics. This wastewater requires a multiple-stage treatment process to meet discharge regulations. Treatment processes commonly used for coal conversion wastewaters include solvent extraction, steam stripping, and biological oxidation and nitrification. An additional concern with these wastewaters is the presence of color. High levels of color are common in coal conversion wastewaters, even subsequent to secondary treatment. Since the discharge of colored water presents an environmental concern as discussed above, the need for economical, effective methods to remove this color exists. The objective of this research is to evaluate color removal from a coal conversion wastewater by solvent extraction, adsorption, and biological methods.

DESCRIPTION OF WASTEWATER

The Great Plains Gasification Plant (GPGP) is located near the city of Beulah in central North Dakota. This plant is the first commercial-sized facility of this type in the United States. GPGP uses Lurgi dry-ash gasification technology to produce pipeline-quality synthetic natural gas (SNG) from lignite. Their operation produces 3.54 x 10^6 m^3/d at standard temperature and pressure (125 MMSCFD) of SNG. Condensate from this gasification process contains very high concentrations of COD, phenols, and ammonia. GPGP produces approximately 13.6 x 10^6 liters per day of condensate. This condensate is solvent extracted and steam stripped to reduce phenols and ammonia, respectively. The pretreated condensate is referred to as stripped gas liquor (SGL).

The composition of GPGP raw gasification condensate (after tar/oil/water separation) and the SGL are shown in Table 1. The analysis of the raw wastewater is based on one sample, while the analysis of the SGL represents the mean of fourteen 6400-liter (1700 gallon) loads of fresh SGL.

Attempts to identify all the organic components in the gasification condensate have not been successful. An analysis of random samples of SGL in 1984 and 1985 yielded a mean closure of 65.8% for TOC and 65.3% for COD. The remaining constituents of the COD are thought to be due to autoxidized catechol and other unidentified organics.

Color Formation

Freshly collected condensate from a number of gasifiers, including the UND slagging fixed-bed gasifier, the METC gasifier, GPGP gasifiers, and the KILnGAS rotary kiln gasifier, are relatively clear in color. These condensates rapidly become dark in color when cooled and exposed to air. When kept from exposure to oxygen they do not change in color. A fresh sample of KILnGAS condensate has been kept in a sealed serum bottle for approximately three years without a noticeable change in color. A replicate KILnGAS sample in a serum bottle remained clear as well, but darkened overnight after air was injected into the bottle.

The color-causing components are believed to be colloids (polymers) based on the fact that 1) filtration with microporous filters (pore sizes <0.45 μm) removes some of the color bodies, and 2) the color is essentially completely removed when the pH of the water is dropped to <2 and then filtered to remove the black precipitate. If the pH is brought to neutrality without removal of the black precipitate, the precipitate re-dissolves and the color returns as before pH adjustment. This behavior fits that of natural, plant-derived humic acids. Pagenkopf (1978) defined humic acids as "... the portion of soil organic matter that is soluble in base and insoluble in mineral acid." Additionally, he stated that the molecular weights of these compounds ranged from a thousand to many thousands and that the humic acids possess phenolic and carboxylic weak acid groups, conferring on them weak polyprotic acid characters, with pKa values in the range of 3 to 10.

The dihydric phenol, catechol, is believed to be the source of the color in these wastewaters based on research conducted at UNDEMRC. A discussion of some of the evidence documenting this conclusion follows.

TABLE 1

COMPOSITION OF GREAT PLAINS GASIFICATION PLANT GASIFICATION CONDENSATE (mg/L)

Parameter	Raw Gas Liquor[a]	Stripped Gas Liquor[b]
Organics		
COD	21,330	2,770
TOC	6,930	870
BOD_5	-[c]	1,150
Phenol	2,490	10
o-Cresol	450	7
m-Cresol	770	4
p-Cresol	580	4
Methanol	600	320
Ethanol	ND[d]	ND
Acetone	520	ND
2-Propanol	ND	ND
Acetonitrile	130	5
Propanol	ND	ND
2-Butanone	100	ND
Propionitrile	<10	ND
Catechol	180	200
5,5-Dimethylhydantoin	ND	ND
5-Ethyl,5-methylhydantoin	ND	ND
Acetate	490	435
Formate	160	110
Butyrate	ND	30
Propionate	110	20
Inorganics		
TKN (as NH_3-N)	4,200	-
Ammonia (NH_3)	6,060	760
Thiocyanate	10	9
Cyanide	<1	5
Sulfide	46	ND
Thiosulfate	110	8
Sulfate	54	30
Chloride	<5	6
Phosphate	ND	207
Alkalinity (as $CaCO_3$)	17,200	2120
Conductivity (µmohs/cm)	25,600	-
pH	8.6	9.3

[a] Represents a single analysis
[b] Represents the mean of fourteen, 6400-liter loads
[c] Not analyzed
[d] Not detected

Initially, during attempts to identify the missing carbon in a carbon balance of the GPGP condensate UNDEMRC performed analyses for catechol. Catechol numbers were found to decrease rapidly with age of the sample. At the same time, it was noted that the color increased with the age of the sample. It was postulated that the two phenomena were related. Further experiments showed that decreases in both catechol and dissolved oxygen were first order at a pH greater than 8.5.

A synthetic polymer was made by adding 5 g of catechol to 100 mLs of water containing 2 g ammonium hydroxide and enough sodium hydroxide to provide a pH of 8 to 9. This solution was aerated via a fine-bubble diffuser and stirred for one week. The resulting dark solution was acidified to pH 1 with HCl, producing a fine black precipitate. The precipitate was collected by filtering through a fritted glass filter and air drying. Polymers were collected by the same technique from aged GPGP condensate and aged UNDEMRC gasification condensate (Wiltsee 1986a and 1986b).

Infrared spectra were compared for the synthetic polymer and the polymers isolated from GPGP and UNDEMRC condensates. The spectra for the synthetic and GPGP polymers were similar with corresponding absorbances at 3300, 1700, 1600, 1500-1450, 1250, 850, and 750 cm^{-1} (see Figure 1). The UNDEMRC polymer had fewer similar peaks at 3200, 1700, 1600, 1400, and 800 cm^{-1}. The similarities in the IR spectra for these polymers indicate that the overall structure of the polymers are similar.

Molecular weight determinations were performed with the GPGP and synthetic polymers using HPLC size exclusion chromatography. The average molecular weight ranged from 200 to 5000 g/mole for the GPGP polymer and 200 to 2500 g/mole for the synthetic polymer (Wiltsee 1986a). Higher molecular weights for the GPGP polymer are not surprising since the GPGP condensate contains many more organics which undoubtedly are involved in the oxidations, the reaction time is longer for GPGP condensate, and the condensate contains metals (Cu, Fe, and Mg) which are known to be catalytic for humic acid formation (Schnitzer et al. 1984).

Molecular weight determinations were also performed using low-angle laser-light scattering photometry. This analysis resulted in weight average molecular weights approximately 100 times greater than those obtained with size exclusion chromatography. Both analyses were performed with tetrahydrofuran as the solvent, but the size exclusion chromatography used styrene-based molecular weight standards. Both measurements probably contain a great deal of error due to major differences in soluble and non-soluble fractions in the solvent and chemical and physical property differences between the standards and the samples.

Table 2 shows a comparison of the quantity of carbon, hydrogen, and nitrogen in each of the three polymers collected. The analysis was performed using a Perkin-Elmer Model 240 C,H,N analyzer. The gasifier-derived polymers contained as much as 7 times more nitrogen that the synthetic polymer. This would indicate that nitrogen was probably available in a number of reactive forms in the gasification condensate compared to the synthetic mixture where ammonia was the only nitrogen source (Wiltsee 1986b).

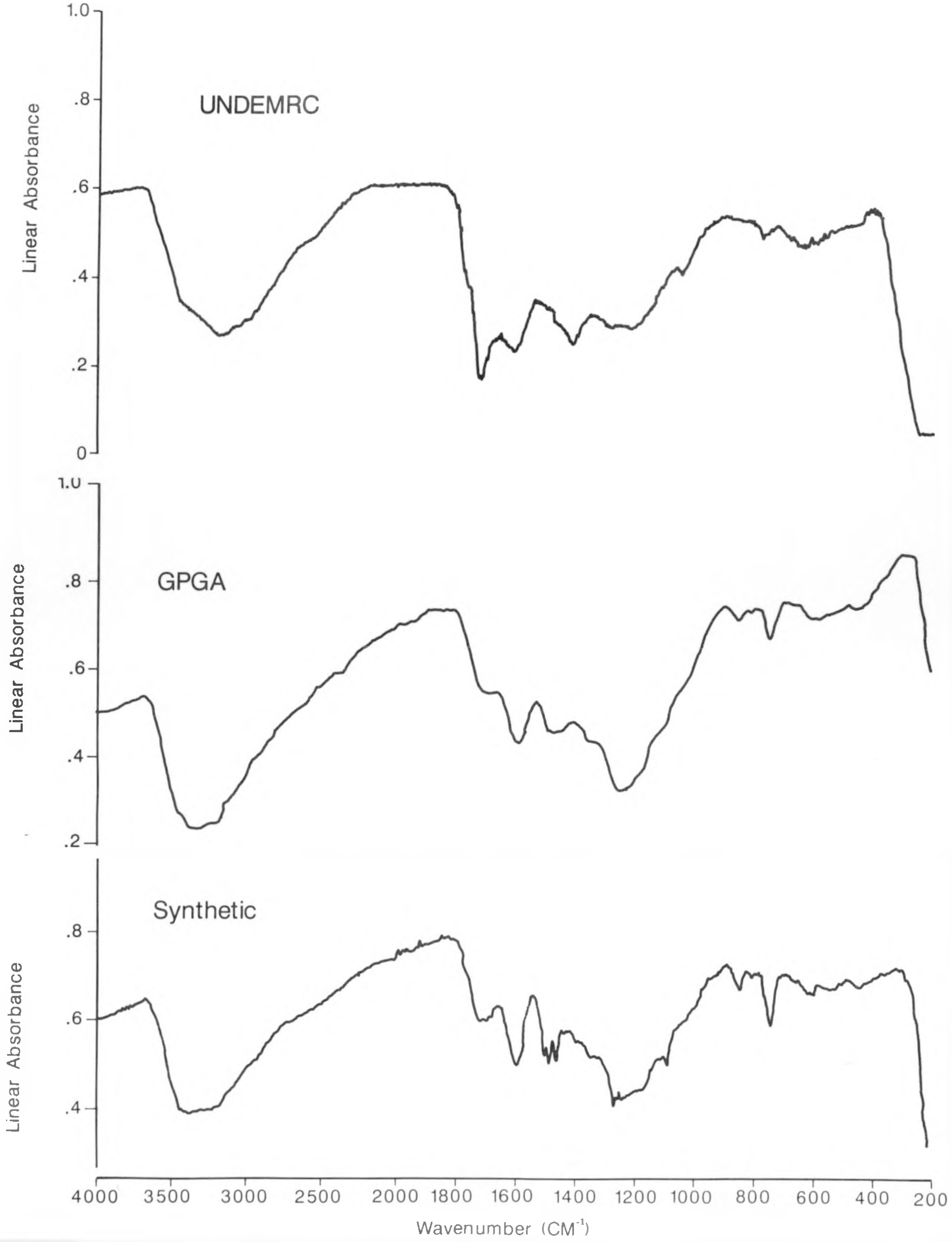


Figure 1. Comparison of infrared spectra from a synthetic catechol polymer and polymers isolated from UNDEMRC and GPGP wastewater.

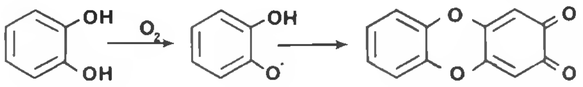
TABLE 2

CARBON, HYDROGEN, AND NITROGEN ANALYSIS OF THE POLYMERS

Polymer	% Dry Weight Carbon	 Hydrogen	 Nitrogen
Synthetic	57.91	3.47	1.21
UNDEMRC	47.68	4.03	8.21
GPGP	38.02	4.64	8.75

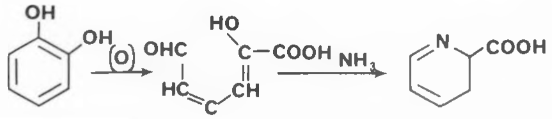
In a ^{13}C-NMR spectrum, catechol has peaks at 145.0, 117.3, and 122.1 ppm. The solid state ^{13}C-NMR spectra of the synthetic polymer and the GPGP polymer are shown in Figure 2. The peaks at 100 to 160 are easily matched with catechol for both the GPGP and synthetic polymer and indicate broad similarities in their aromatic functionalities. In the spectral range from 0 to 120 ppm, there are broad peaks for the GPGP polymer which are absent in the spectra for the synthetic polymer. The contribution in the aliphatic carbon region of the spectra for the GPGP polymer is expected due to the presence of a variety of aliphatic substituted catechols present in the condensate.

Assuming that catechol is the basic unit of these polymers, a structure and reaction mechanism can be postulated. Under acidic and alkaline conditions, catechol oxidizes via a radical to give a quinone. Quinones can then form unstable addition products that may polymerize to form dimers (Equation 1). Under some conditions, oxidation may open the ring to form muconic acid, one of the humic acids.



(1)

The oxidation of catechol is dependent on pH and may be accelerated by trace amounts of copper, iron, or magnesium, all of which are present in gasification condensate. At pH >8.5, the kinetics of the catechol polymer formation are first order, in the absence of nitrogen compounds, with respect to dissolved oxygen and catechol (Schnitzer et al. 1984). It is at these higher pH levels that phenols with two or more hydroxy groups can react with ammonia to give nitrogen-containing polymers. These compounds are formed after the oxidation of catechol to give a mono-aldehyde. A further reaction with ammonia results in a heterocyclic compound (Equation 2, Giesking 1975).



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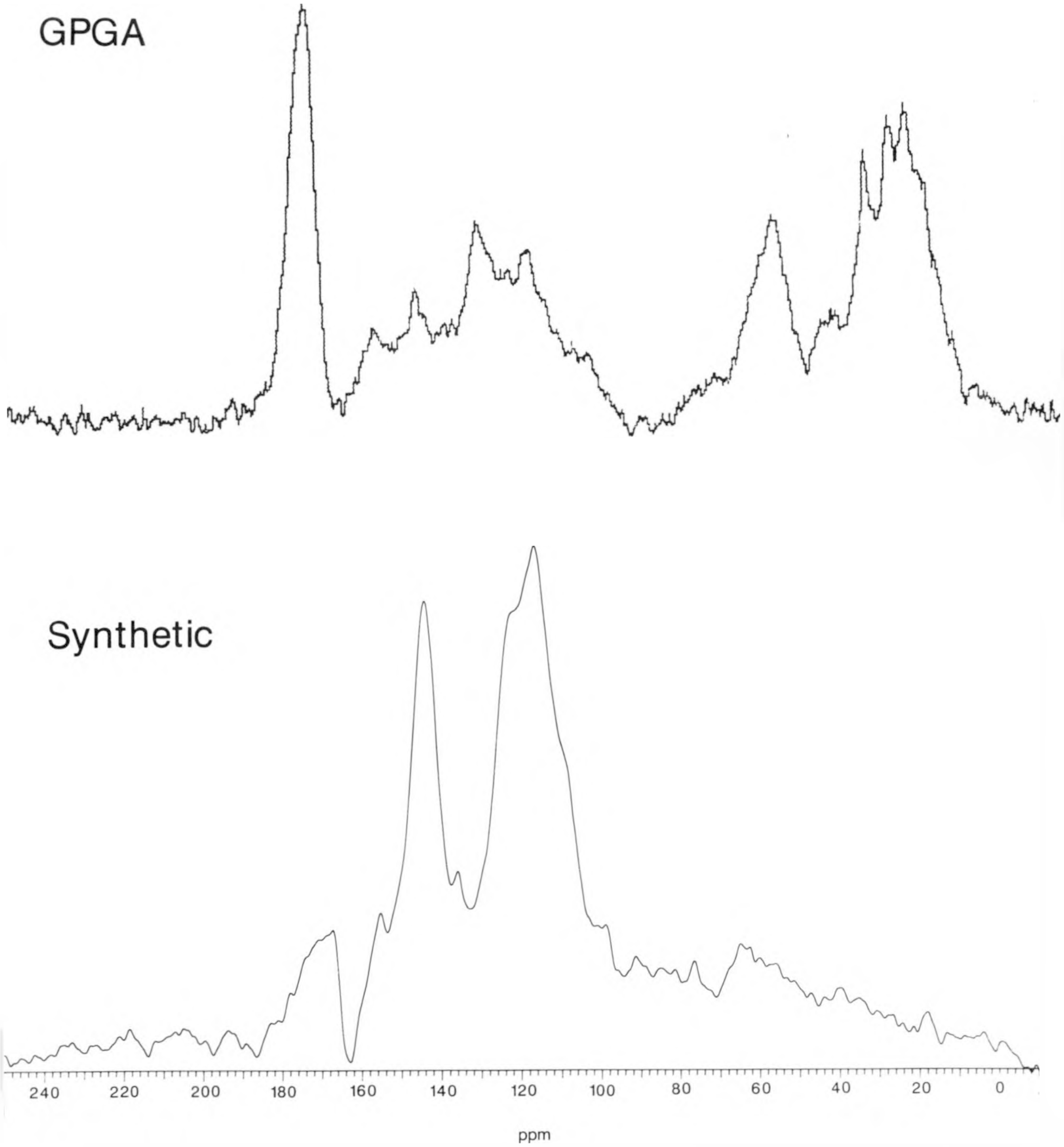
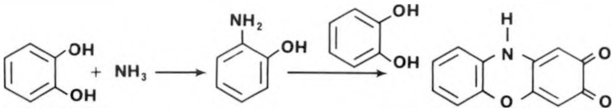


Figure 2. Comparison of ^{13}C-NMR spectra for a synthetic catechol polymer and a polymer isolated from GPGP wastewater.

In the absence of oxygen and the presence of ammonia, the hydroxyl group may be replaced with ammonia. When oxygen is added, the aminophenol may react with the starting compound to form a dimer (Equation 3, Giesking 1975).



(3)

In summary, the results of the chemical investigations of the "natural" and synthetic polymers have shown that catechol, oxygen, ammonia, and other wastewater components react to form polymers similar to natural soil humic acids that impart a dark color to the wastewater. These polymers are probably very similar to those found in pulping wastewaters, where lignin-derived compounds result in a colored wastewater.

COLOR REMOVAL

Removal of these catechol-derived color-causing polymers is not achieved through most conventional wastewater treatment processes. The polymers are not volatile, soluble in polar solvents, or degraded by bacteria and therefore are not removed by steam stripping, solvent extraction, or activated sludge treatment, respectively. Activated carbon will remove the polymers, but high doses and long contact times are generally required, which result in unfavorable economics of removal.

Solvent extraction of the color from synthetic fuels wastewater was reported by Neufeld (1985). They solvent extracted UNDEMRC gasifier wastewater with methylisobutylketone (MIBK) in a 36-stage continuous, countercurrent flow Scheibel liquid-liquid extraction column at a solvent-to-water ratio of 1:11.5. Phenolics were reduced 99.4% at an influent concentration of 3812 mg/L. The "brown humic color" was "noticeably" reduced, but not quantified. A trial solvent extraction of KILnGAS condensate at EMRC with MIBK revealed that the color was concentrated in the emulsion formed at the solvent/water interface. When this emulsion was separated and broken, the color had partitioned into the aqueous phase. This suggested an inexpensive technique for color removal/concentration.

George et al. (1986) reported investigations on the biological removal of color from a pretreated coal gasification wastewater (UNDEMRC slagging fixed-bed gasifier condensate). The basis for biological removal of these components is that the humic acids are similar in structure to lignin. A number of fungi, in particular wood-rot fungi, possess some very powerful and relatively non-selective enzymes that are oxygenases and peroxidases that are active against lignin. George et al. (1986) investigated the MyCoR process, a patented biological process for removal of color from pulping wastewaters. This process uses the fungus Phanerochaete chrysosporium attached to a rotating biological contactor. The optimum conditions stated for this process are 40°C, pH of 4.5 and 100% oxygen.

George et al. (1986) found color removal of about 50% with a 25% solution of wastewater, and 32% removal with a 100% wastewater. The fungal process had a rather limited lifetime related to the initial color concentration of the feed. Decolorization decreased exponentially with increasing wastewater (and color) concentration. The kinetics of decolorization were estimated using the method of Kincannon, resulting in a Umax of 2.5 lb color/day/1000 ft^2 and a Km of 2.7 lb color/day/1000 ft^2.

The fact that the color removal quickly reached a maximum, and rapidly declined, plus the fact that the fungal biomass darkened throughout treatment indicates that adsorption, and not biological degradation was probably a major mechanism. Additionally, the conditions used in this process, such as 40°C, 100% oxygen, and a one-day hydraulic retention time, are not very economical.

Fukuzumi (1980) conducted screening studies on decolorization and defoaming of pulping wastewaters. He found that several white-rot fungi had good capabilities to remove color. Color removal was enhanced by the addition of saccharides. Color removal was found to be due to degradation or partial oxidation rather than adsorption.

TESTING METHODOLOGY

SOLVENT EXTRACTION

One hundred mLs of room temperature bio-treated, filtered (0.45 μm pore size membrane filter) GPGP SGL was added to a 250 mL extraction funnel. Twenty-five mLs of solvent were added and the funnel was capped and shaken vigorously for one minute. The funnel was placed upright in a ringstand and allowed to stand for one minute or until the solvent and water phases separated. Gross observations, including the changes in color, the amount of emulsion, etc., were noted. After phase separation, the emulsion, if any, was removed and a sample of both the water and solvent phases were collected for further analyses. The emulsion was broken by using a ultrasonicator cleaner. Once the emulsion was broken, the separate phases were collected for analysis.

Solvents for testing were selected based on providing a range of polarities, since polarity is the major factor governing solubility. The dielectric constant, or the measure of the ability of a material to store electric potential energy under the influence of an electric field, was chosen as a measure of polarity (Mellan 1950). Other useful solvent properties considered were low solubility in water and ability to form solvent/water emulsions. Benzene and methylene chloride have been noted for their emulsion-forming capabilities in aqueous extractions (Gordon and Ford 1972).

The chemical and physical properties of the selected solvents are shown in Table 3. Figure 3 shows the relationship between the dielectric constant and the log percent water solubility of the selected solvents. The dielectric constant of water, which is highly polar, is 80.37 at 20°C.

TABLE 3

CHEMICAL AND PHYSICAL PROPERTIES OF THE SELECTED SOLVENTS

Solvent	MW	Dielectric Constant[a]	Specific Gravity[b]	Solubility in Water[c]
n-Hexane	86.2	1.89	0.660	13
Benzene	78.1	2.28	0.879	1,780
DIPE	102.2	3.88	0.730	9,000
n-Butyl acetate	116.2	5.01	0.882	14,000
Ethyl acetate	88.1	6.02	0.901	79,000
Methylene chloride	84.9	9.08	1.325	20,000
MIBK	100.2	13.11	0.802	17,000
2-Butanol	74.1	15.80	0.808	125,000
1-Butanol	74.1	17.80	0.810	77,000

[a] All reported at 20°C, except DIPE, ethyl acetate, and 2-butanol, which were measured at 25°C.
[b] Reported at 20/4°C.
[c] mg/L at 20°C.

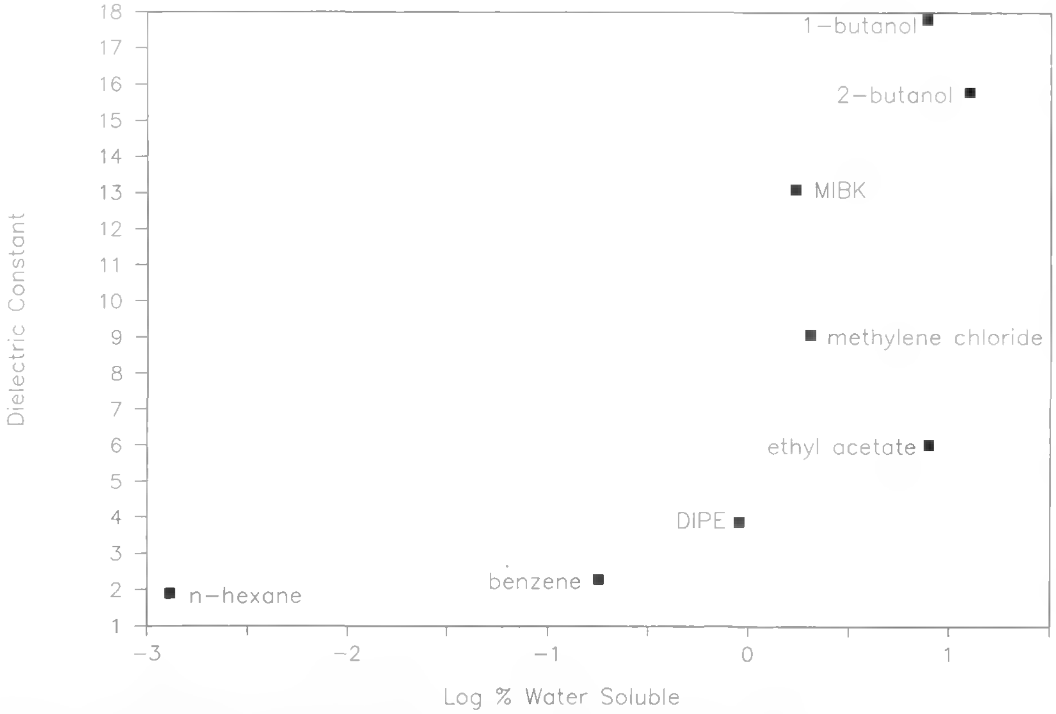


Figure 3. Relationship between the dielectric constant, a measure of solvent polarity, and the log percent water solubility for the test solvents.

ADSORPTION

Various doses of sized and dried or as-received adsorbents were mixed with 50 to 100 mLs of filtered, room temperature bio-treated SGL in 250 mL erlenmeyer flasks. The flasks were capped to prevent evaporation and placed on a gyratory shaker at 100 rpm for 24 hours. An aliquot was then removed from each flask and filtered through 0.45 µm pore size membrane filters to remove the adsorbent. The filtrate was then analyzed for color. The effect of pH was evaluated for some adsorbents at the as-received pH (about 6.5) and at pH values of 5 and 10 for each adsorbent dose. Doses tested ranged from 0.05 to 5.0 grams adsorbant per 100 mLs of wastewater. Adsorption isotherms were plotted for each adsorbent at the various pHs tested. Coefficients describing the adsorption for each adsorbent were calculated and compared.

A number of activated carbons were chosen for testing including the following: F-100 and F-400 from Calgon Carbon Corporation, Pittsburgh, PA; Hydrodarco C and R, and Darco S-51 and GFP from American Norit Company, Jacksonville, FL; and Nuchar S-A from Westvaco, Covington, VA. Two coals, a lignite from the Indian Head Mine, ND, and a lignite from the Freedom/Beulah Mine, ND, were tested. The coal samples were obtained from the UNDEMRC coal sample bank and had been stored under argon.

Manufacturer-supplied data on the activated carbons are shown in Table 4. The surface area is a BET measurement using nitrogen gas. The iodine number is an estimate of the quantity of pore with sizes in the >10 angstrom range, or for adsorption of low molecular weight compounds. The molasses index is a measure of molasses' decolorizing ability and indicates pore sizes >28 angstroms, or adsorption of high molecular weight compounds. The source indicates the starting material in the manufacture of the carbon. Carbons made from bituminous coals tend to have smaller pore sizes than those made from lignites. The pH is that of an aqueous slurry of the carbon (EPA 1973).

A hemic peat originating from a Minnesota peat bog, air-dried and sized to <60 mesh, was tested. A number of ashes, obtained from the UND Coal By-Products Utilization Laboratory stocks, were used in the color removal testing. These ashes are identified in Table 5 and the available characterization data are shown in Table 6.

The adsorption data from the isotherm tests with activated carbons and ashes were analyzed using the Freundlich isotherm. The Freundlich equation for adsorption isotherms is given in Equation 5.

$$\frac{X}{M} = KC^{1/n} \tag{4}$$

Where X = amount of color adsorbed,
M = weight of carbon,
C = unadsorbed concentration of color left in solution,
K = constant,
n = constant.

TABLE 4

MANUFACTURERS' DATA ON THE ACTIVATED CARBONS TESTED

Property	Calgon F-100	Calgon F-400	Darco S-51	Darco GFP	Hydroarco C	Hydroarco R	Nuchar S-A
Total Surface Area BET (m^2/g)	850-900	950-1050	650	600	575	575	1400-1800
Iodine Number (min)	850	1000	NR[a]	NR	NR[a]	NR	900
Effective Size (mm)	0.8-1.0	0.55-0.75	NR	NR	NR	NR	NR
Molasses Index	NR	NR	95	NR	80	40	14
Source	bituminous	bituminous	NR	lignite	lignite	lignite	NR
pH	NR	NR	acidic	alk	alk	alk	acidic

[a] Not reported.

TABLE 5

SOURCE OF ASHES USED IN COLOR-REMOVAL TESTS

Identification	Location/Production	Coal Type
Gentleman Station (GS)	Southerland, NE 1,278 MW	Wyoming, Subbit.
Great Plains Gasification Plant (GPGP)	Beulah, ND 125 MMSCFD SNG	Indianhead lignite
Coal Creek Station (CC)	Underwood, ND 506 MW	ND lignite
Pleasant Prairie (PP)	Pleasant Prairie, WI 1,160 MW	Wyoming Subbit.
Columbia Portage (CP)	Portage, WI 463.6 MW	Montana or Wyoming subbit.

This equation is linearized by taking the log of both sides of the equation to give Equation 5. When the log X/M is plotted against the log C, the slope of the line gives 1/n and is obtained from the y-intercept.

$$\log X/M = \log K + 1/n \log C \tag{5}$$

The isotherm test can show whether or not a particular degree of removal can be effected by adsorption alone. It also can show the approximate adsorptive capacity of the carbon for the application (EPA 1973). For isotherms which fit the Freundlich equation, the following interpretations have been suggested (Adams et al. 1981).

High K and high n - indicates high adsorption throughout the concentration range tested.

Low K and high n - indicates low adsorption throughout the concentration range tested.

Low n (steep slope) - indicates high adsorption at strong solute concentrations and low adsorption at low solute concentrations.

TABLE 6

COMPOSITION OF ASHES TESTED[a]

Component[b]	GS	GP	CC	PP	CP
SiO_2	35.9	26.6	44.7	35.3	34.0
Al_2O_3	18.3	12.9	15.7	20.4	20.4
Fe_2O_3	5.2	7.8	7.4	5.6	5.2
SO_3	2.76	1.14	1.50	2.65	2.82
CaO	25.5	20.6	20.7	25.4	26.2
MgO	5.2	7.8	5.3	5.8	4.8
Na_2O	2.6	7.2	0.5	1.6	2.2
K_2O	0.3	0.6	1.2	0.3	0.3
Moisture	0.04	1.38	0.03	0.07	0.01
Loss on Ignition	0.22	10.28	0.03	0.52	0.19
Specific Gravity	2.58	N/A[c]	2.54	2.51	2.63
Date Collected	3/88	1/88	3/88	4/88	3/88

[a] Analysis was by ASTM methods for ash (x-ray fluorescence analysis for elemental composition).
[b] Units are % dry weight except for specific gravity (unitless) and date collected (month/year).
[c] Not analyzed.

BIOLOGICAL REMOVAL

The fungi used are listed in Table 7. The identified fungi were chosen based on the research of Fukuzumi (1980). The fungi were obtained from the American Type Culture Collection (ATCC), with the exception of a fungus isolated from coal slurry. The slurry fungus was isolated at UNDEMRC from a lignite slurry prepared via the UNDEMRC hot-water drying process. All fungi manipulations were performed using standard microbiological aseptic, axenic methods. Fungal inoculation, transfer, and sampling was performed in a Class II biological safety cabinet. Samples for color analysis were filtered through 0.20-μm pore size syringe filters to remove fungal hyphae and spores from the water.

TABLE 7

FUNGI USED FOR COLOR-REMOVAL TESTING

Species	Source
Phanerochaete chrysosporium	ATCC #34541
Polyporus anceps (Dichomitus squalens)	ATCC #13242
Poria latemarginata (Oxyporus latemarginata)	ATCC #24649
Tramates versicolor (Coriolus versicolor)	ATCC #12679
Aspergillus sp.	ATCC #20243
Slurry fungus	Lignite slurry

The fungi were maintained in YM (Yeast Maintance) broth (Difco). Biological removal tests were performed in 100 mLs of filtered (0.45 μm), biotreated SGL supplemented with Yeast Nitrogen Broth (Difco) at a rate of 0.67 g/L with 1% or 2% dextrose added. The pH of the SGL was adjusted to 5.5 in order to be more conducive for growth of the fungi. Inoculation of the test flasks was done with bacteriological loops, transferring a small, but substantial, piece of hyphae. The flasks were weighed so that corrections could be made for evaporation. All cultures were incubated at room temperature with gentle shaking (80 rpm on a gyratory shaker). Incubation continued for 15 days.

COLOR ANALYSIS

Color analysis was performed on samples that had been filtered (true versus apparent color). In addition, since the pH of the solution has a very large impact on the measured color, the pH was adjusted to 7.6 prior to analysis, as recommended by Standard Methods (APHA 1985). The absorbance of the filtered water was measured at 465 nm in a quartz cell (1 cm path length) with a Perkin-Elmer Model 200 UV-Vis spectrophotometer.

The samples from the biological removal testing could not be analyzed by the spectrophotometric method since dextrose also absorbs at 465 nm. Therefore these samples were analyzed using a Hach color comparator, which gives results in the equivalent of APHA platinum-cobalt (PtCo) color units.

RESULTS AND DISCUSSION

SOLVENT EXTRACTION

The results of the solvent extraction tests for color removal are shown in Figure 4, which shows the percent transmittance in the water after solvent extraction versus the dielectric constant of the test solvents. The percent transmittance (%T) was that of samples diluted 1:36 with deionized water and

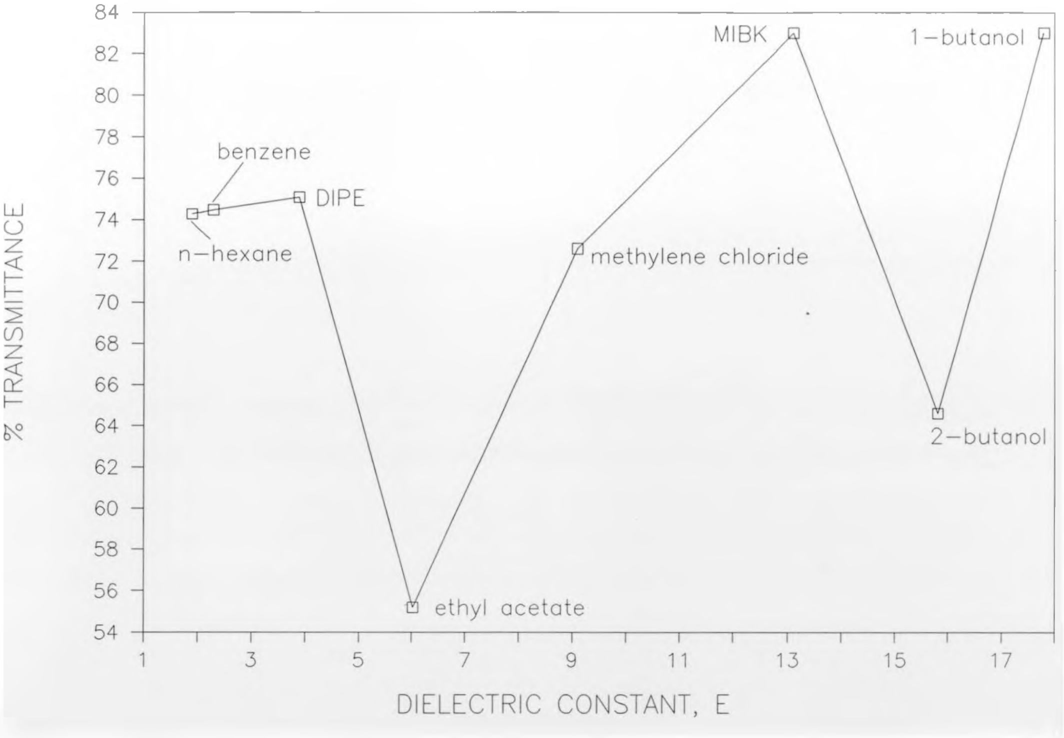


Figure 4. Percent transmittance (465 nm) versus solvent dielectric constant (a measure of polarity) after solvent extraction at a solvent-to-water ratio of 1:4 (v/v) in bio-treated GPGP stripped gas liquor. The initial transmittance was 73.9%.

measured at 465 nm. The untreated wastewater had a %T of 73.9. Thus, the data show that the solvents n-hexane, benzene, DIPE, and methylene chloride had little or no effect; ethyl acetate and n-butyl acetate increased the %T (absorption by the solvent at the wavelength tested); and MIBK and 1-butanol removed some color.

Even though some color was removed by two of the solvents, the quantity removed is very small considering the high solvent-to-water ratio used (1:4). In addition, it is apparent that those solvents with larger dielectric constants are better at color removal. However, increases in dielectric constant (solvent polarity) also reflect increases in water solubility of the solvents as shown in Figure 3. MIBK, however, is often commercially used in solvent extraction processes for the removal of phenolics (Chem-Pro process) and might be expected to provide some color removal when used with colored gasification wastewaters.

ADSORPTION

The adsorption isotherm data for the activated carbons tested are shown in Table 8. The figures showing the raw data for these isotherms are in the Appendix. These data are listed by decreasing K, thus the carbon with the

TABLE 8

COMPARISON OF FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION OF COLOR USING COMMERCIALLY AVAILABLE ACTIVATED CARBONS LISTED BY DECREASING K

Sorbent	pH	K	n	R^2
Hydrodarco C	7	2.16 E-02	0.393	0.969
Hydrodarco C	5	8.85 E-03	0.348	0.977
Darco S-51	7	8.67 E-03	0.369	0.746
Hydrodarco C	10	6.78 E-03	0.446	0.991
Darco S-51	5	6.24 E-03	0.502	0.768
Darco S-51	10	5.00 E-03	0.397	0.858
F-400	10	1.86 E-03	0.523	0.934
F-400	5	1.43 E-03	0.538	0.975
F-400	7	1.14 E-03	0.604	0.973
F-100	10	9.04 E-04	0.600	0.978
F-100	5	8.31 E-04	0.479	0.994
F-100	7	7.45 E-04	0.484	0.988
Nuchar S-A	5	7.24 E-04	0.676	0.994
Nuchar S-A	7	4.73 E-04	0.829	0.539
Nuchar S-A	10	4.63 E-04	0.601	0.855

highest adsorption are at the top. The values of the n constant for all activated carbons listed in Table 8 are very similar, ranging from a low of 0.348 to a high of 0.829, with a mean and standard deviation of 0.519 ± 0.124. The K values had a broader range, from a high of 2.16 x 10^{-2} to a low of 4.63 x 10^{-4}, with a mean and standard deviation of 4.38 x 10^{-3} ± 5.5 x 10^{-3}. The effect of pH is apparent from the data. For Darco and Nuchar activated carbons, the acidic-to-neutral pHs had greater K values, while for the Calgon carbons, the opposite is observed. These effects are probably related to the size of the color-body at the test pH as a function of the pore size of the test carbon. Overall the lignite-based carbons are better at decolorizing this wastewater.

R^2 is the correlation coefficient for least squares linear regression. In a perfect correlation the $R^2 = \pm 1$. The R^2 values for the activated carbons are, for all carbons but a few test conditions, quite good. This indicates that the observed data for these carbons fits the Freundlich equation quite well. Freundlich isotherm data are not available for the Darco GFP and the Hydrodarco R activated carbons. These carbons removed 100% of the color at all test doses except the lowest (0.05 g/100 mLs) and did not fit the Freundlich equation. They would likely have a high K, and a very low n, indicating high adsorption at strong solute concentrations and low adsorption at dilute solute concentrations.

The mechanism of adsorption of color by these ashes is not known. However, unburned coal which has been devolatilized (activated), as well as metal oxides such as those of aluminum, iron, and magnesium may adsorb color.

The coal-derived ashes that were tested were obtained from a variety of power plants. In addition, the ash from the gasifiers at the Great Plains Gasification Plant was tested. The results of these tests, as Freundlich isotherms constants, are shown in Table 9. The isotherms are shown in the Appendix. The K constant varied over 6 orders of magnitude from a high of 192 to a low of 8.93 x 10^{-4} with a mean and standard deviation of 13.61 ± 47.67. The n constant varied over 7 orders of magnitude from a high of 0.447 to a low of 5.14 x 10^{-8} with a mean and standard deviation of 9.86 x 10^{-2} ± 1.26 x 10^{-1}. These data indicate that many of the ashes have greater adsorption than the activated carbons, but the ashes are more likely to have high adsorption at strong solute concentrations and low adsorption at low solute concentrations (as indicated by the small n values).

TABLE 9

COMPARISON OF FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION
OF COLOR USING COAL-DERIVED ASHES
LISTED BY DECREASING K

Sorbent[a]	pH	K	n	R^2
PP	5	1.92 E+02	4.08 E-06	0.960
GP	10	1.12 E+01	5.14 E-08	0.997
CC	10	8.25 E-01	5.97 E-04	0.967
CC	7	2.04 E-01	2.80 E-03	0.905
CC	5	6.45 E-02	8.78 E-03	0.897
PP	7	6.37 E-02	6.59 E-03	0.925
CP	10	4.90 E-02	1.15 E-02	0.992
CP	5	3.29 E-02	2.03 E-02	0.974
GS	10	1.03 E-02	1.01 E-01	0.865
GS	5	7.44 E-03	2.17 E-01	0.964
CP	7	2.87 E-03	1.79 E-01	0.996
GS	7	2.68 E-03	8.80 E-02	0.926
GP	7	1.55 E-03	1.33 E-01	0.977
GP	5	9.34 E-04	2.64 E-01	0.979
PP	10	8.93 E-04	4.47 E-01	0.872

[a] PP = Pleasant Prairie; GP = Great Plains Gasification Plant; CC = Coal Creek; CP = Columbia Portage; GS = Gentleman Station. Coal source and production are shown in Table 5. Ash characterization is shown in Table 6.

The effect of pH on adsorption can be seen by noting the position of the same ash in the table at the test pHs. Changes in pH had little effect on adsorption by the Coal Creek (CC) ash, but strongly affected the adsorption by the Pleasant Prairie ash (PP). The adsorption by other ashes was affected by pH to a lesser extent. The high R^2 values observed indicate that overall the Freundlich equation fit the observed adsorption very well.

An additional mechanism that should be considered is metal-catalyzed chemical oxidation. The identification of the mechanism was beyond the scope of this study.

Lignites from the Freedom/Beulah and Indian Head mines and a hemic peat removed no detectable quantities of color under the test conditions.

BIOLOGICAL REMOVAL

The fungi-inoculated wastewater samples were incubated for a period of 15 days. Samples were removed for color analysis at time 0, 4, 8, and 15 days. The starting color was approximately 3000 PtCo units. The results of these analyses are shown in Figures 5 and 6 with 1% and 2% added dextrose (alpha-D-glucose), respectively. These data show that approximately 60% of the color is removed by Day 4 for both doses of dextrose, although slightly less color is removed with 2% dextrose added.

For the treatment with 1% added dextrose, color removal continued for all fungi except *D. squalens*, which reached a plateau after Day 4 and *T. versicolor*, which actually increased in color (decreased color removal). In the treatments with 2% dextrose added, color removal continued after Day 4 for all fungi except *D. squalens* and *T. versicolor*, which had increased color. The highest color removals observed were approximately the same for both 1% and 2% dextrose added, but there was considerably more variability among the fungi at the 1% concentration.

Photographs showing the fungal cultures, as they were after 10 days of incubation, compared to a sterile control are in the Appendix.

Significant color removal was also observed in a separate experiment, performed for a different project and purpose. In order to evaluate denitrification potential of biomass from a biological reactor, some biomass was added to a serum bottle to which GPGP stripped gas liquor, to which 2 g/L potassium nitrate and 1% dextrose had been added. The bottle was purged with oxygen-free nitrogen to remove traces of oxygen and sealed with a butyl rubber septum. The bottle was then incubated at 30°C and the quantity of gas produced from the reduction of the nitrate was measured over a period of days. As the incubation progressed, it was noted that the color decreased significantly.

After the incubation was completed, after approximately 2 weeks, the remaining color was analyzed and compared to the starting color. Over 80% of the color was removed, as measured by the change in absorbance at 465 nm at a pH of 7.6. No color removal had been noted in continuous denitrification tests conducted using the same wastewater (GPGP).

Figure 5. Time course of color removal by fungi from bio-treated GPGP stripped gas liquor with 1% dextrose (glucose) added.

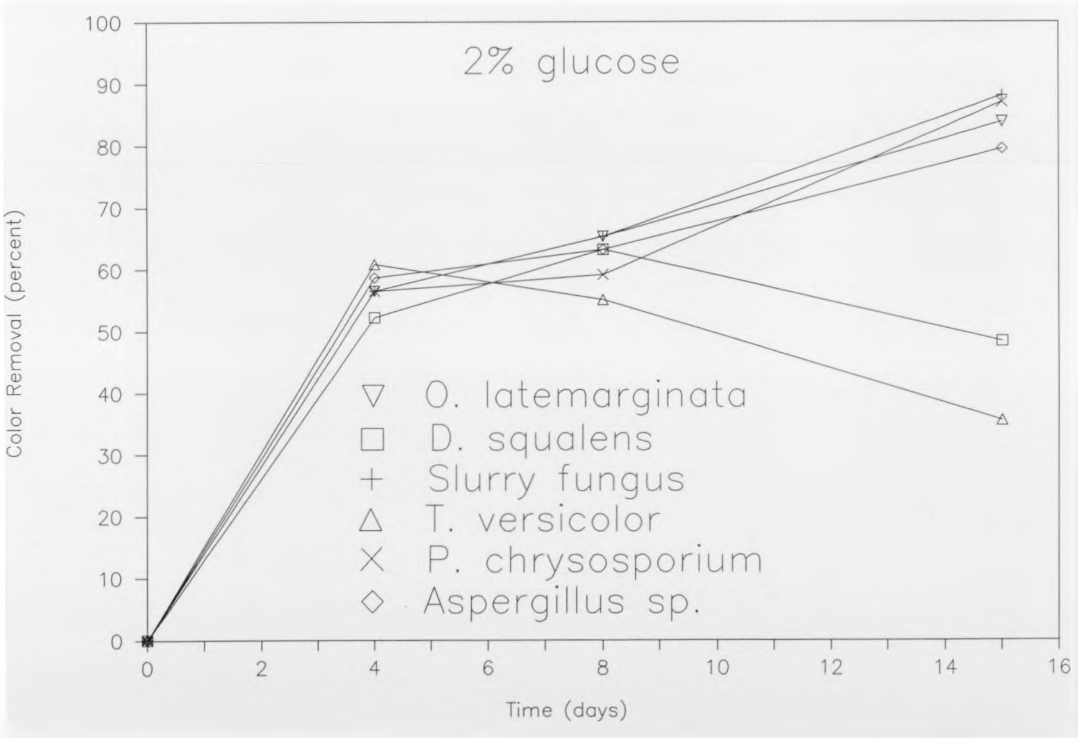


Figure 6. Time course of color removal by fungi from bio-treated GPGP stripped gas liquor with 2% dextrose (glucose) added.

EFFECT OF pH

Since it was known from previous studies on the color components, and also by definition as humic acids, that the color component would form a precipitate under acidic conditions, this was evaluated. The titration curve for one liter of GPGP bio-treated stripped gas liquor is shown in Figure 7, using 0.1 N HCl. The color remaining in solution at various pHs after settling, filtration, and adjustment of the pH up to 7.6 is shown in Figure 8. This figure shows that the humic acids/color components precipitate out at a pH of about 3.2, although some color is removed at pHs of less than 5. Approximately 4 mLs of 0.1 N HCl/L wastewater would be required to precipitate the color in this case. This would scale up to 11.1 mLs concentrated sulfuric acid per 1000 liters of wastewater (42 mLs/1000 gallons). Considerably more acid would likely be required if the wastewater was not pretreated to the same extent as was used in this case.

The titration curve for neutralizing the GPGP wastewater after removal of the color components is shown in Figure 9 as mLs of 0.1 N NaOH per liter. The quantity of NaOH required to raise the pH from 3.0 to 7.0 is estimated as 3 mLs 0.1 N/liter (12 mg NaOH/liter, 12 g NaOH/1000 liters, or 45.4 g/1000 gallons).

SUMMARY OF CONCLUSIONS

1. Significant color removal cannot be expected via solvent extraction. Some removal can be obtained with certain solvents if the design includes removal and separation of solvent/water emulsions.

2. Activated carbons provided good removal with the best results from those carbons that are manufactured from lignites (large pore sizes and high molasses index).

3. Most of the ashes tested provided a surprisingly high level of color removal. The mechanism of color removal via ash is not known, but probably is a combination of adsorption and oxidation. The ability of ash to remove the color provides a synfuels plant with a cheap, throwaway adsorbant.

4. No color removal was observed with two lignites or with a hemic peat.

5. Biological removal was obtained with all of the fungi tested. It is not known if significant fungal removal could be obtained using SGL that had not been bio-treated. If this is possible, a method could be developed for removal of color and BOD in a combined system. Much additional research is required prior to the application of fungal methods to the removal of color.

6. Significant biological removal of color was observed in a batch denitrification test. No biological removal of color was observed in continuous denitrification tests with the GPGP SGL. This method may also have promise for scaleup, but needs much additional research. It is likely that, when deprived of alternative substrates, some oxidation of the color components is possible under denitrifying conditions.

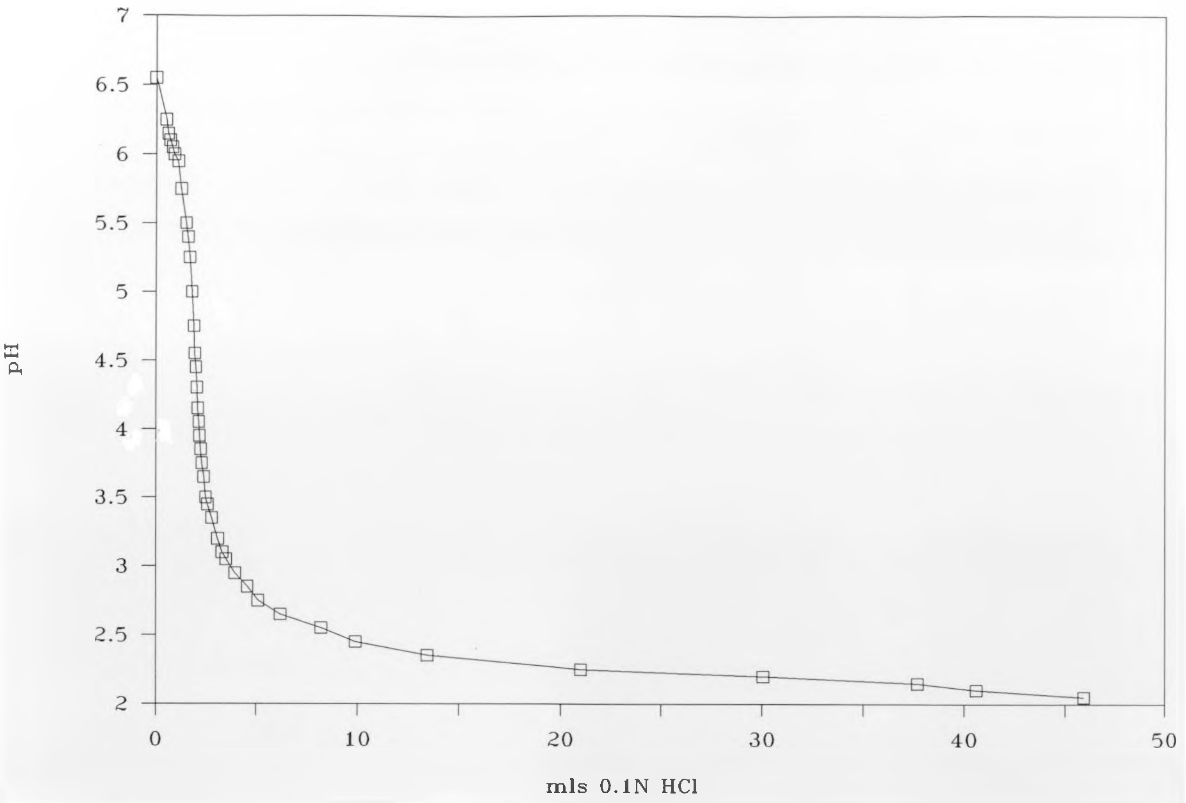


Figure 7. Titration of one liter of Great Plains Gasification Plant bio-treated stripped gas liquor with 0.1 N HCl.

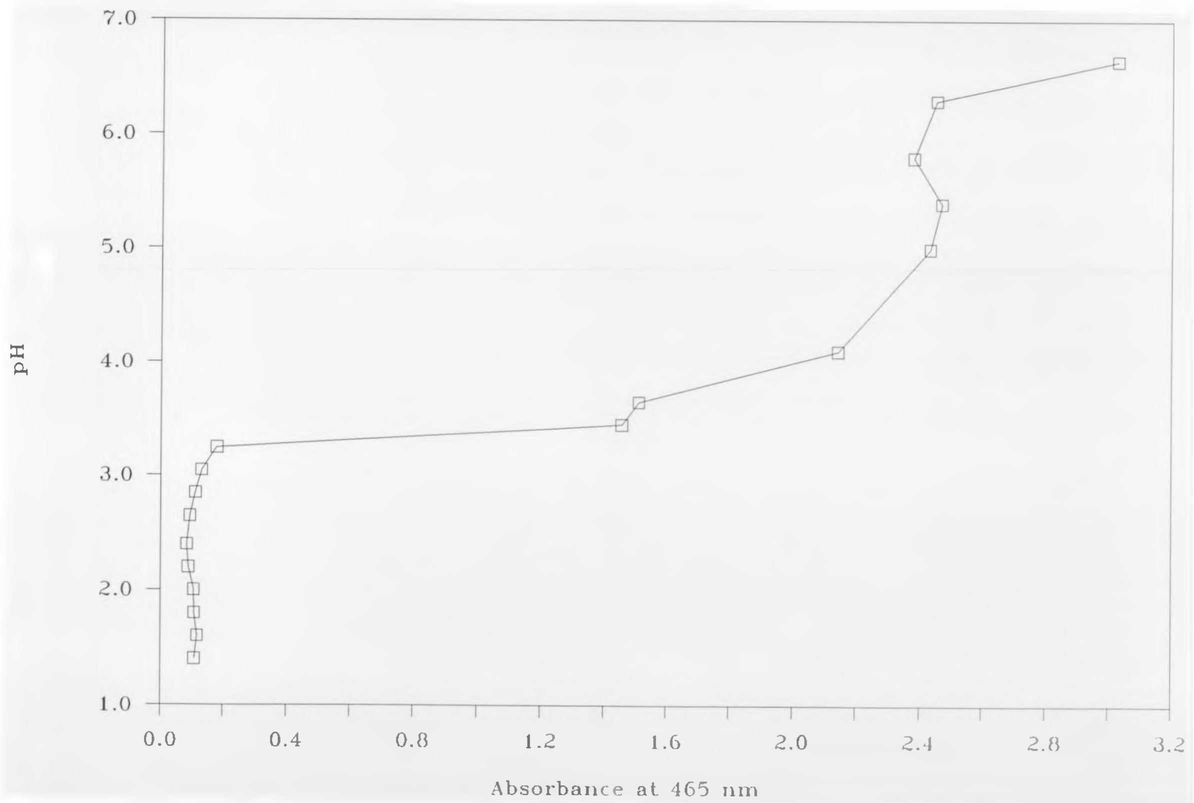


Figure 8. Color remaining in the Great Plains Gasification Plant Liquor, measured as absorbance at 465 nm, after acid addition, removal of precipitate, and neutralizing to pH 7.6.

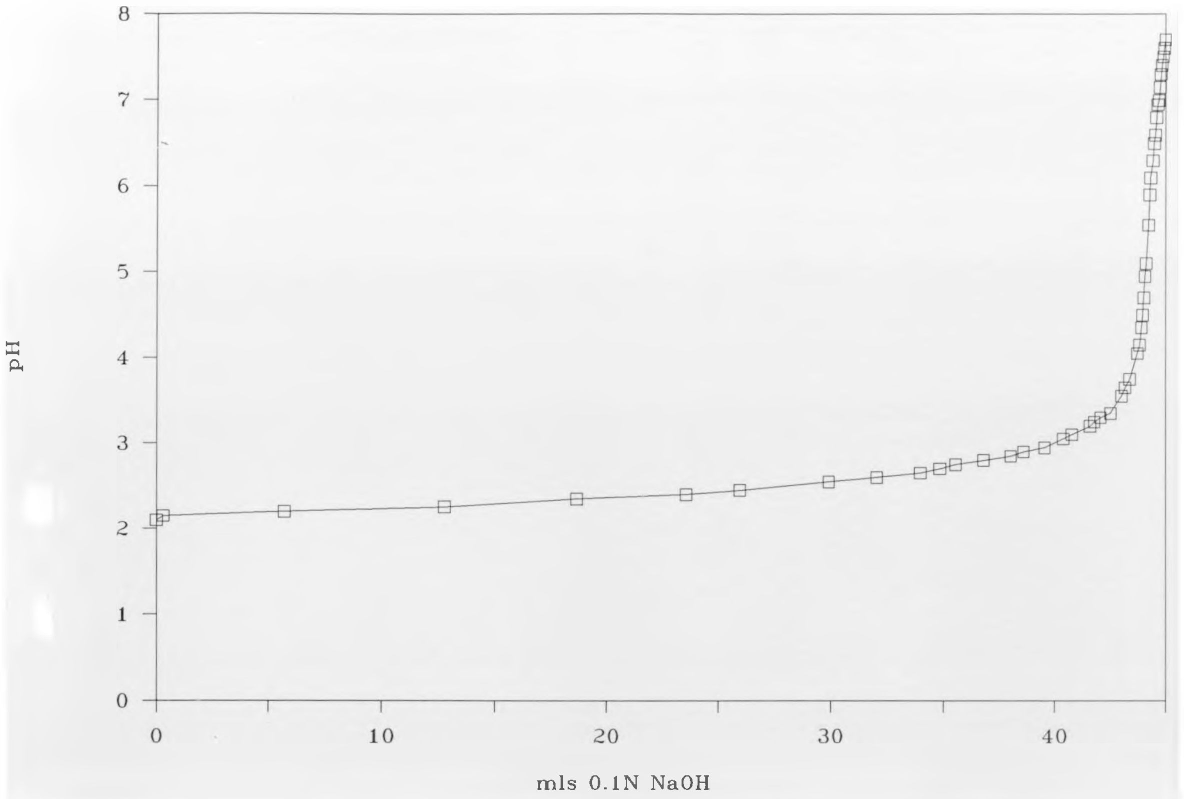


Figure 9. Titration of one liter of Great Plains Gasification Plant bio-treated stripped gas liquor with 0.1 N NaOH after acidification and removal of the precipitate.

7. Acidifying the SGL to a pH of about 3 causes the color components to precipitate. This technique could only be economically applied after significant pretreatment to reduce the buffering capacity of the SGL. Moreover, the increase in dissolved solids via this method may be undesirable.

8. Since the color components require oxygen to form, a method could be developed to prevent the formation and still treat the wastewater. One technique might be to prevent air/oxygen exposure during solvent extraction and steam stripping and utilize anaerobic biological treatment. Anaerobes can readily degrade catechol and other phenolics to methane and carbon dioxide.

ACKNOWLEDGMENTS

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APPENDIX

FREUNDLICH ADSORPTION ISOTHERMS FOR THE REMOVAL OF COLOR FROM GREAT PLAINS GASIFICATION PLANT BIO-TREATED STRIPPED GAS LIQUOR

AND

PHOTOGRAPHS OF THE FUNGAL CULTURES, AFTER 10 DAYS OF INCUBATION, COMPARED TO A STERILE CONTROL

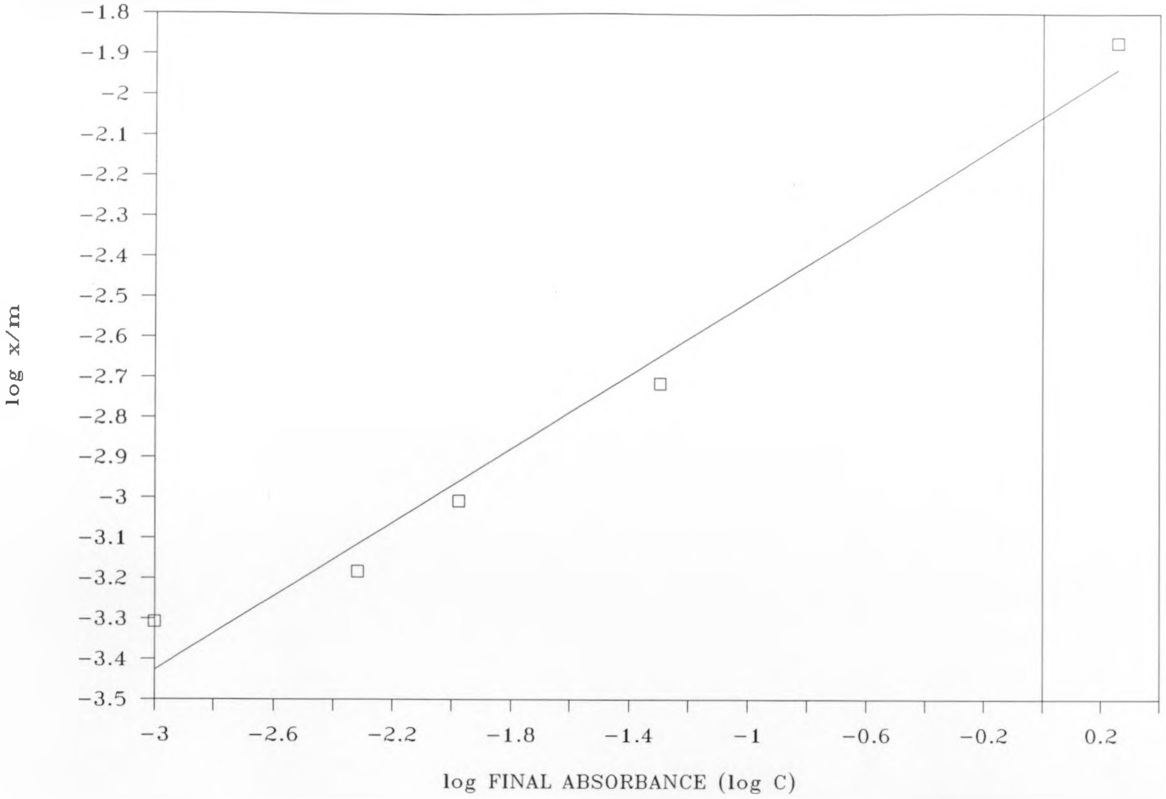

Figure A-1. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using powdered Hydrodarco C activated carbon.

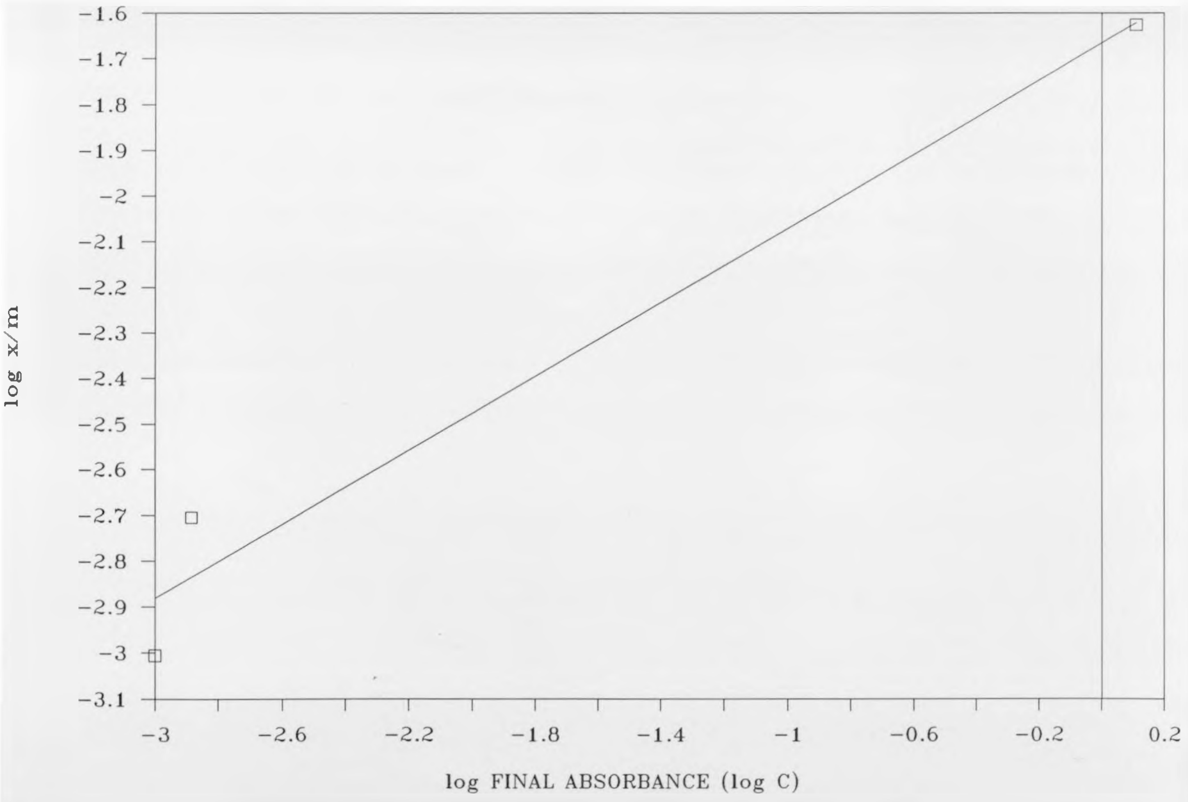

Figure A-2. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using powdered Hydrodarco C activated carbon.

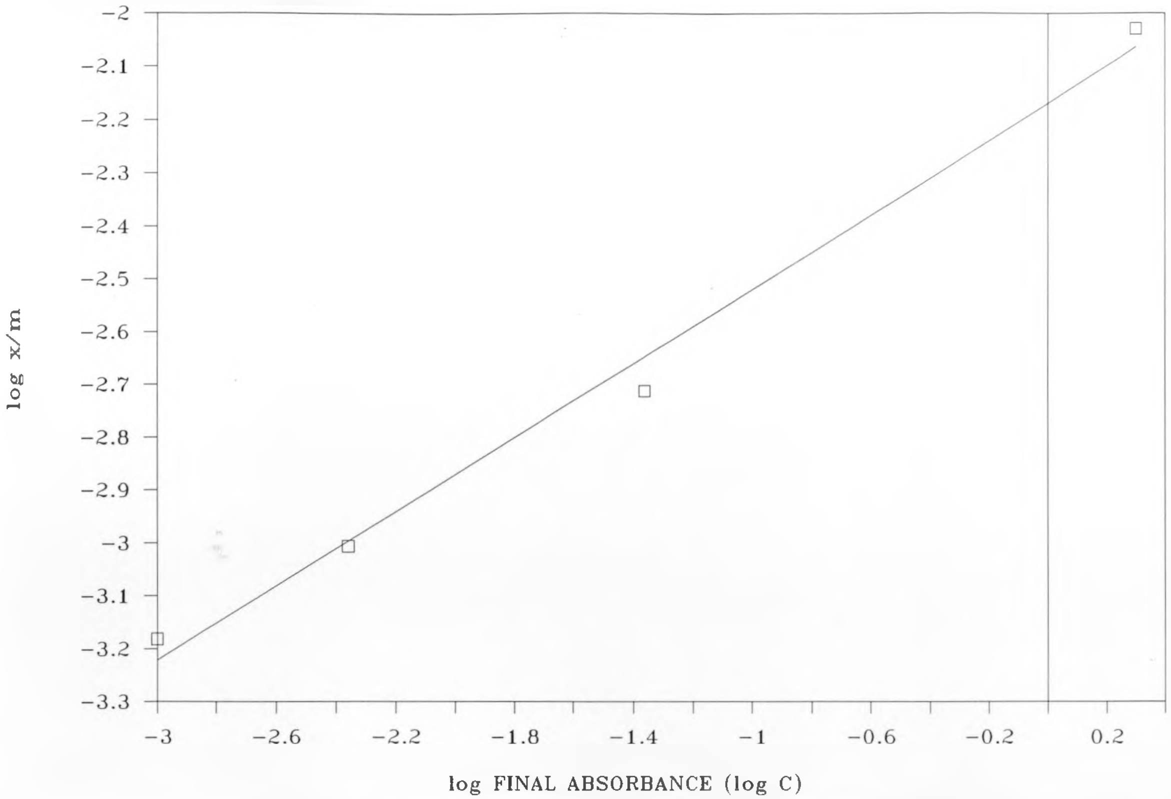

Figure A-3. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using powdered Hydrodarco C activated carbon.

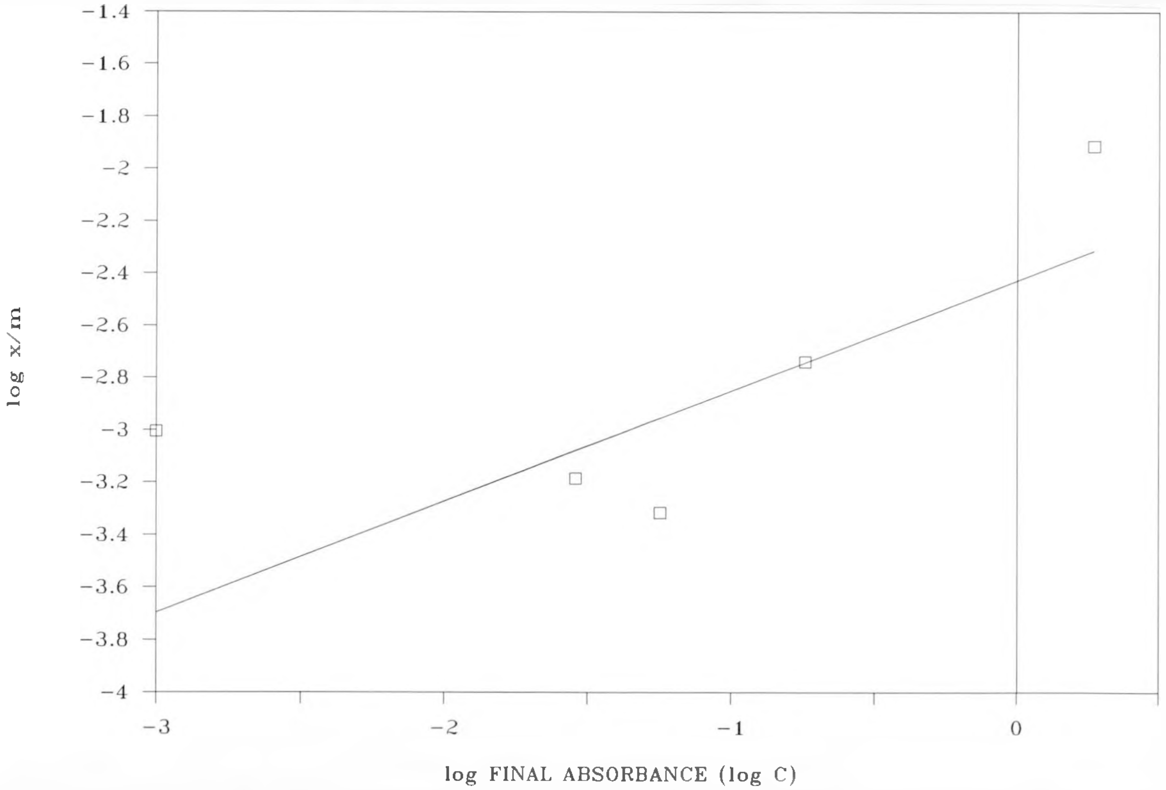

Figure A-4. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using powdered Darco S-51 activated carbon.

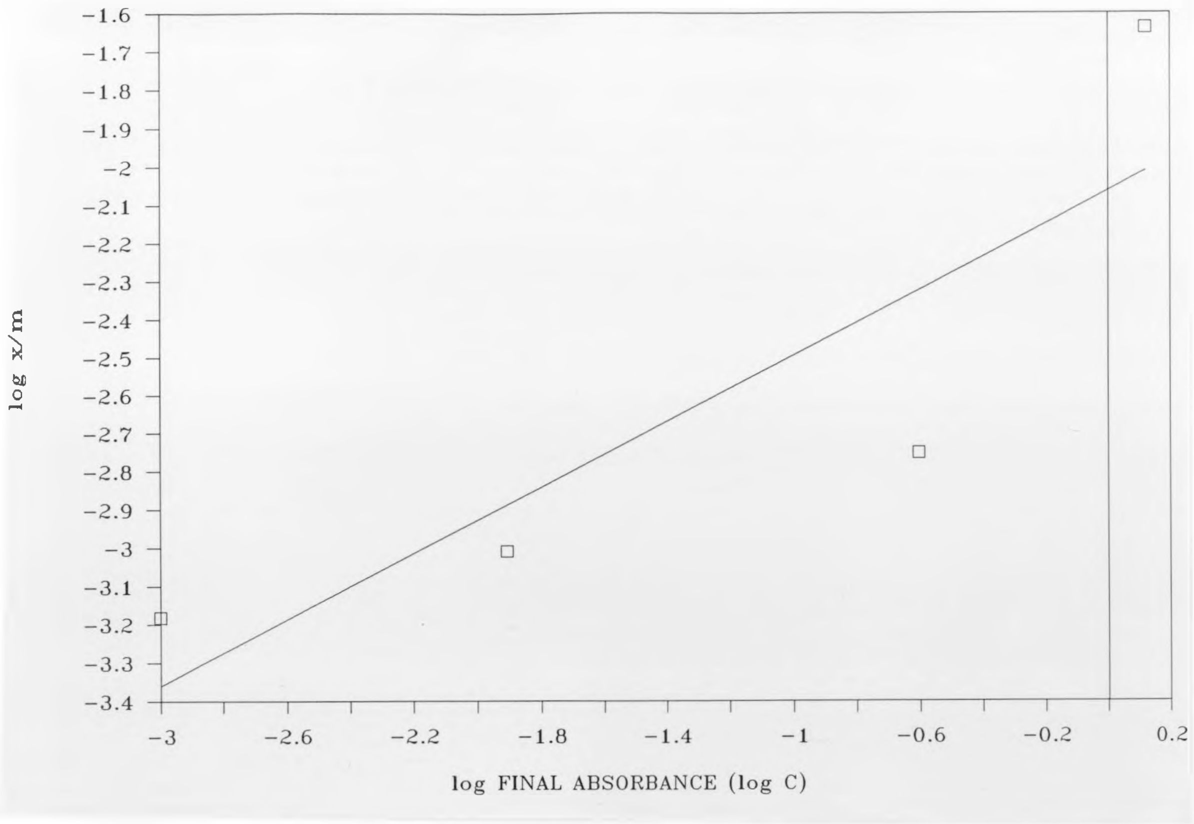

Figure A-5. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using powdered Darco S-51 activated carbon.

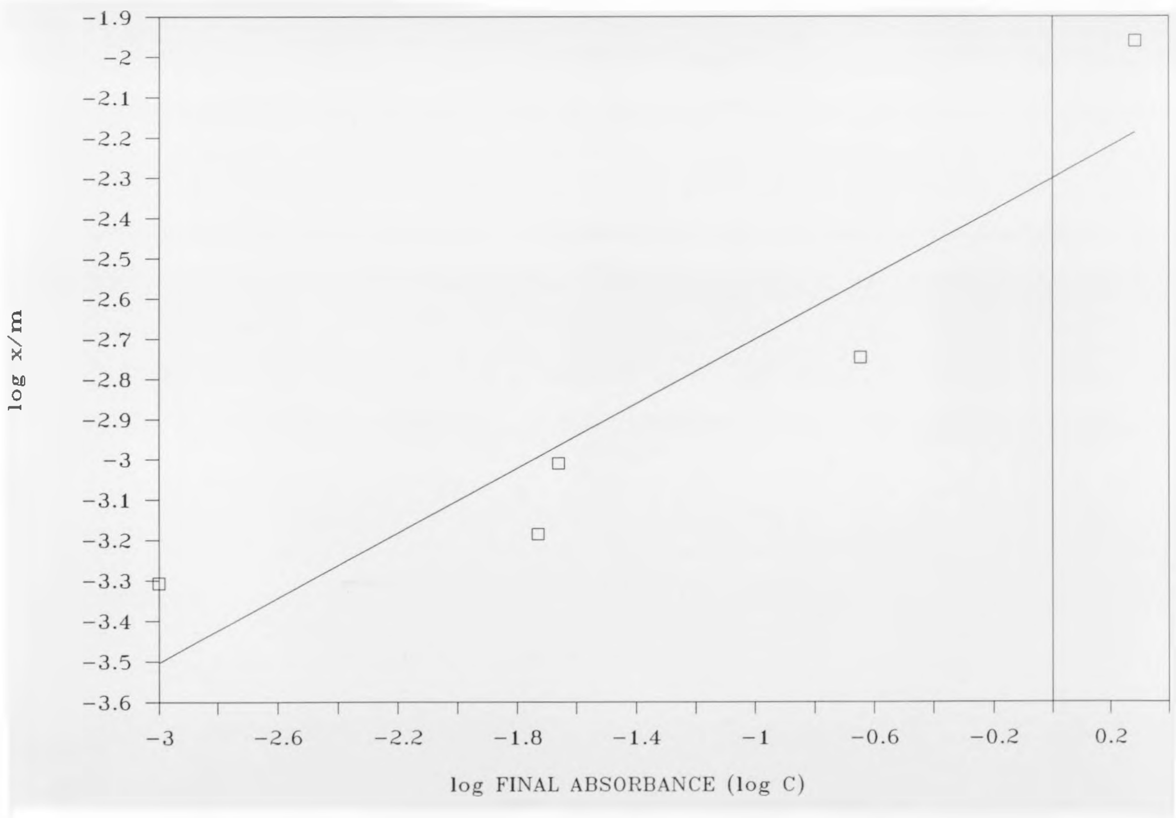

Figure A-6. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using powdered Darco S-51 activated carbon.

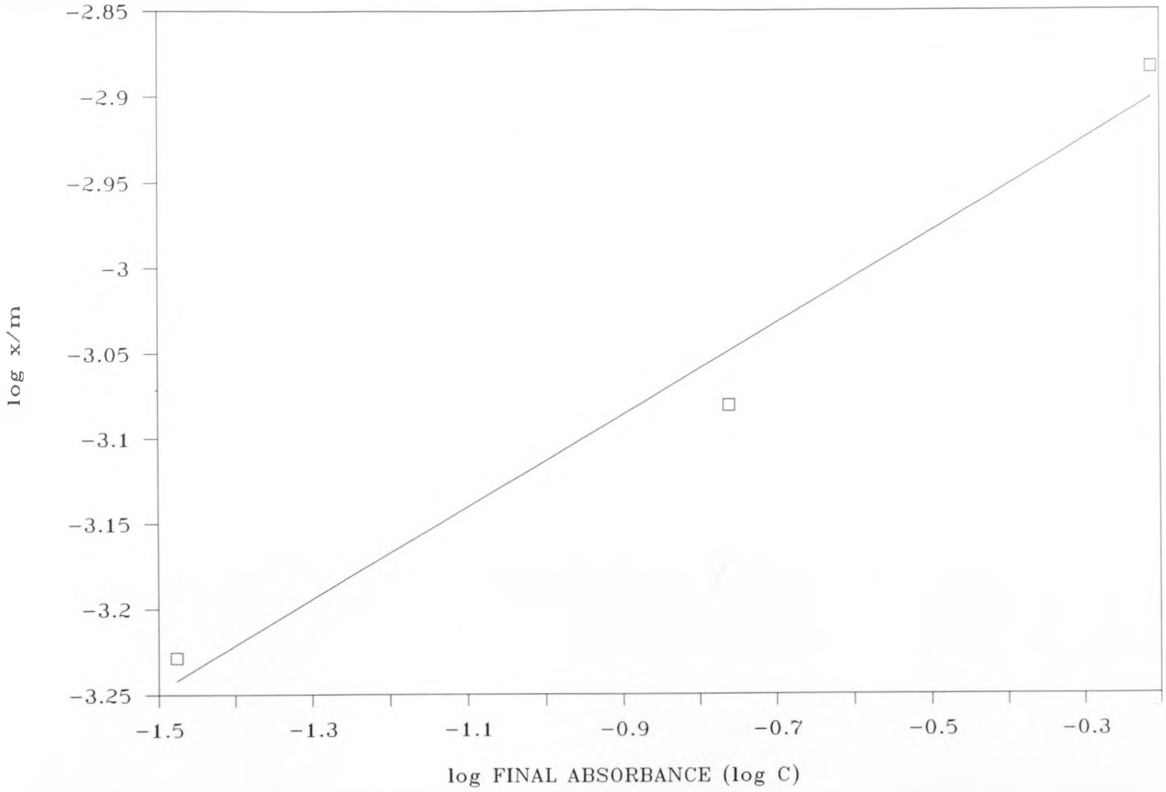

Figure A-7. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using powdered Calgon F-400 activated carbon.

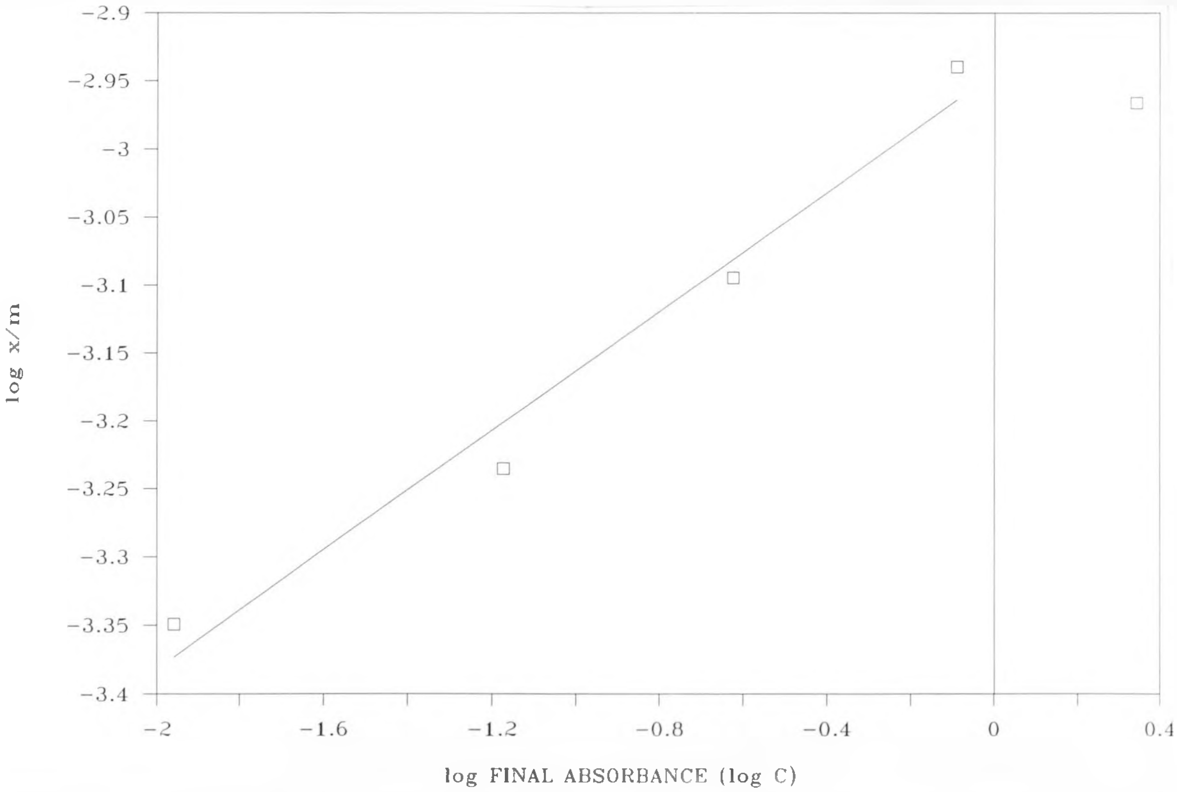

Figure A-8. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using powdered Calgon F-400 activated carbon.

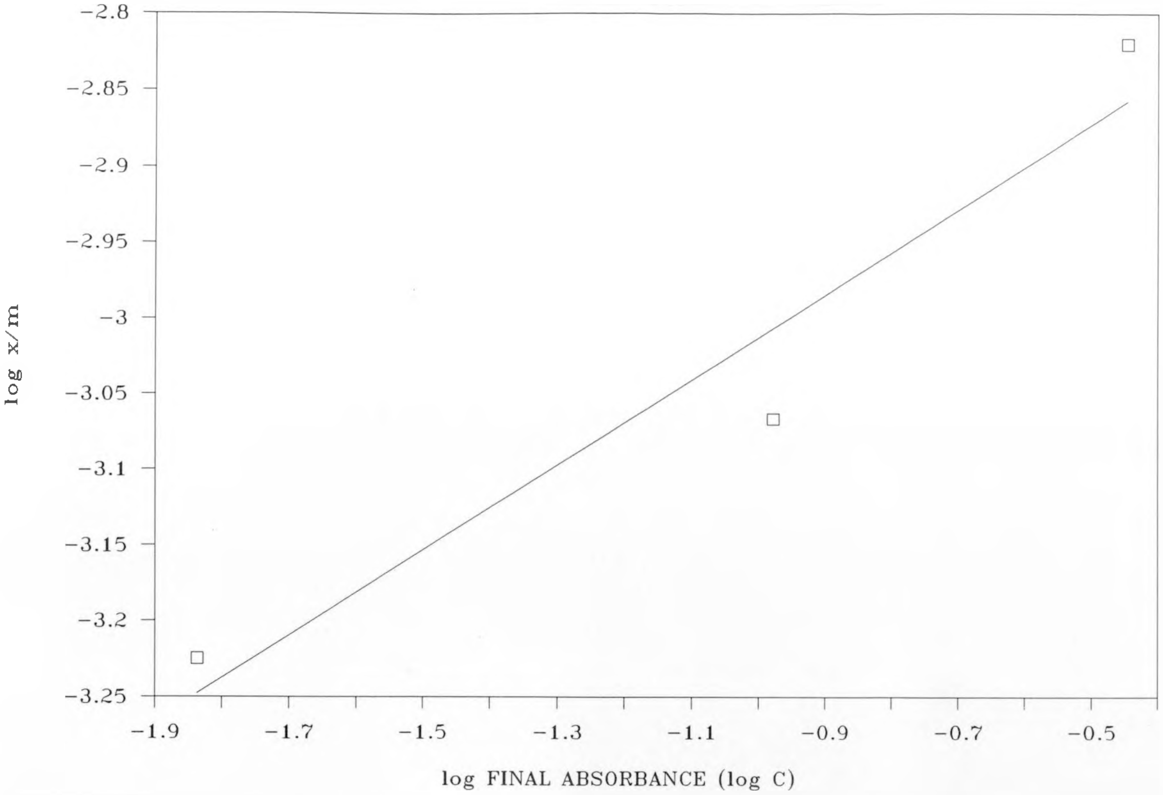

Figure A-9. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using powdered Calgon F-400 activated carbon.

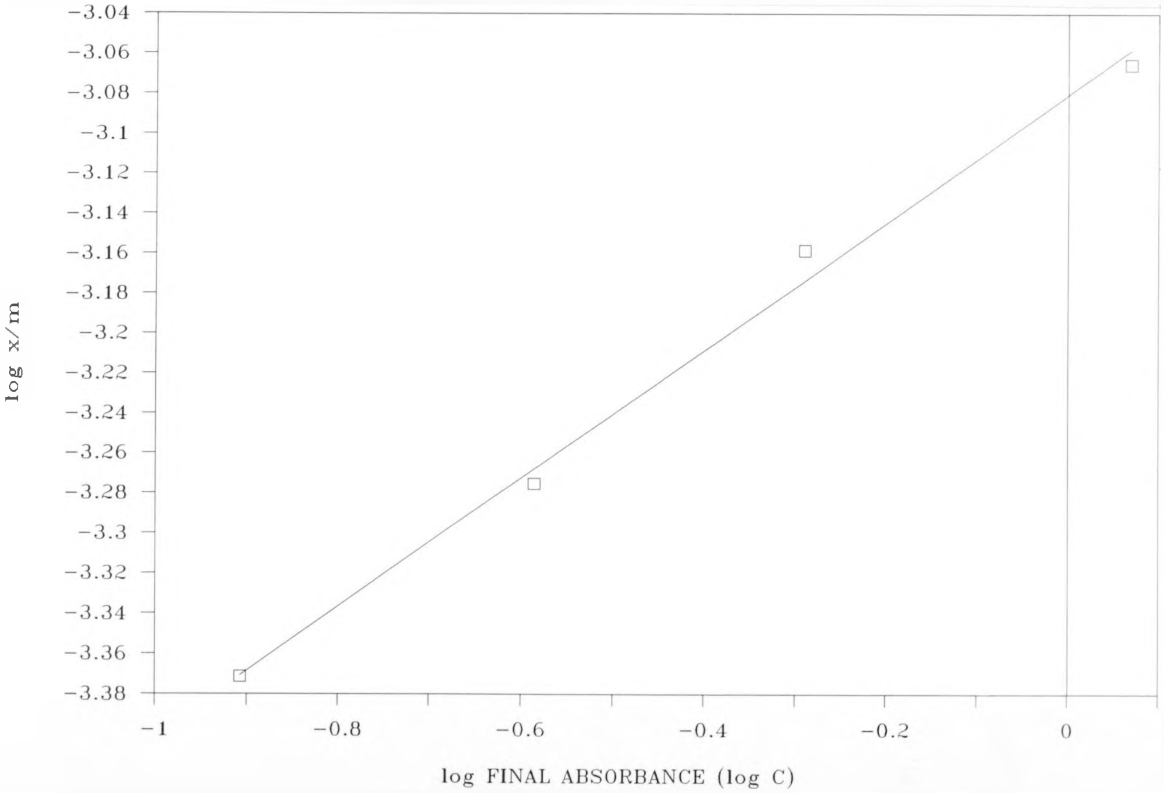

Figure A-10. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using powdered Calgon F-100 activated carbon.

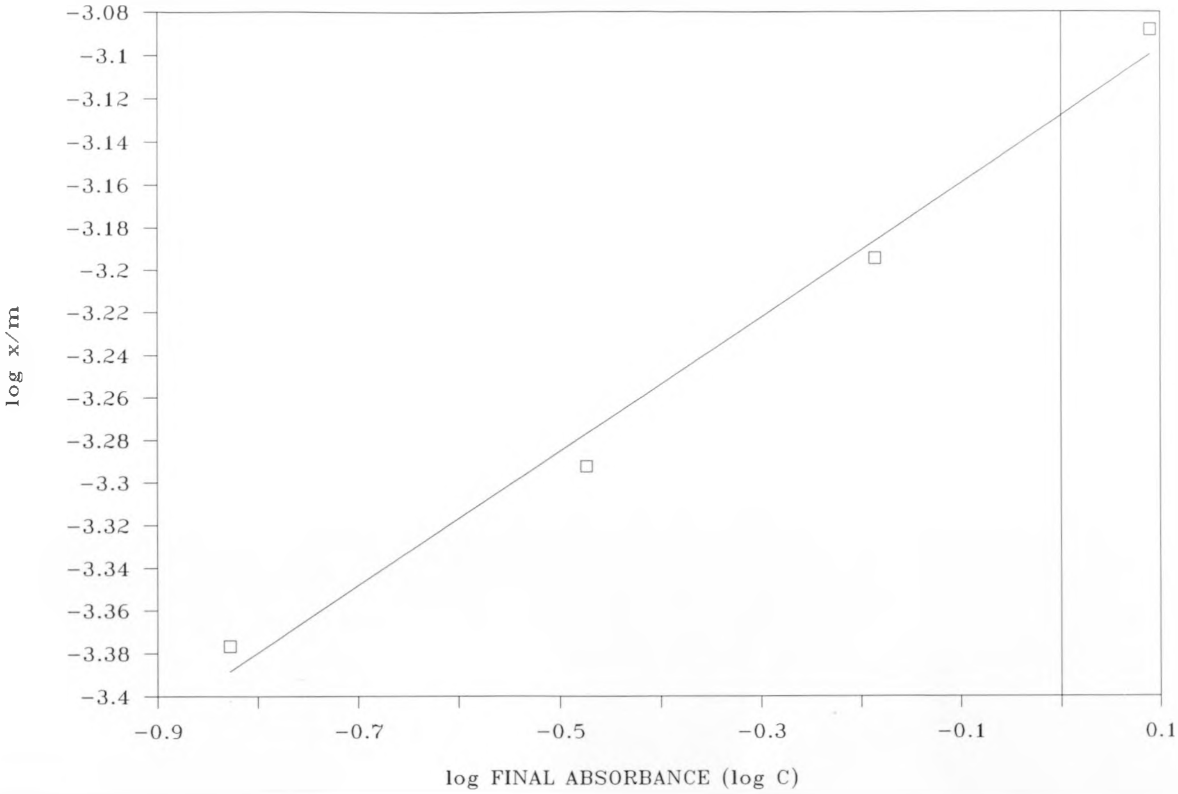

Figure A-11. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using powdered Calgon F-100 activated carbon.

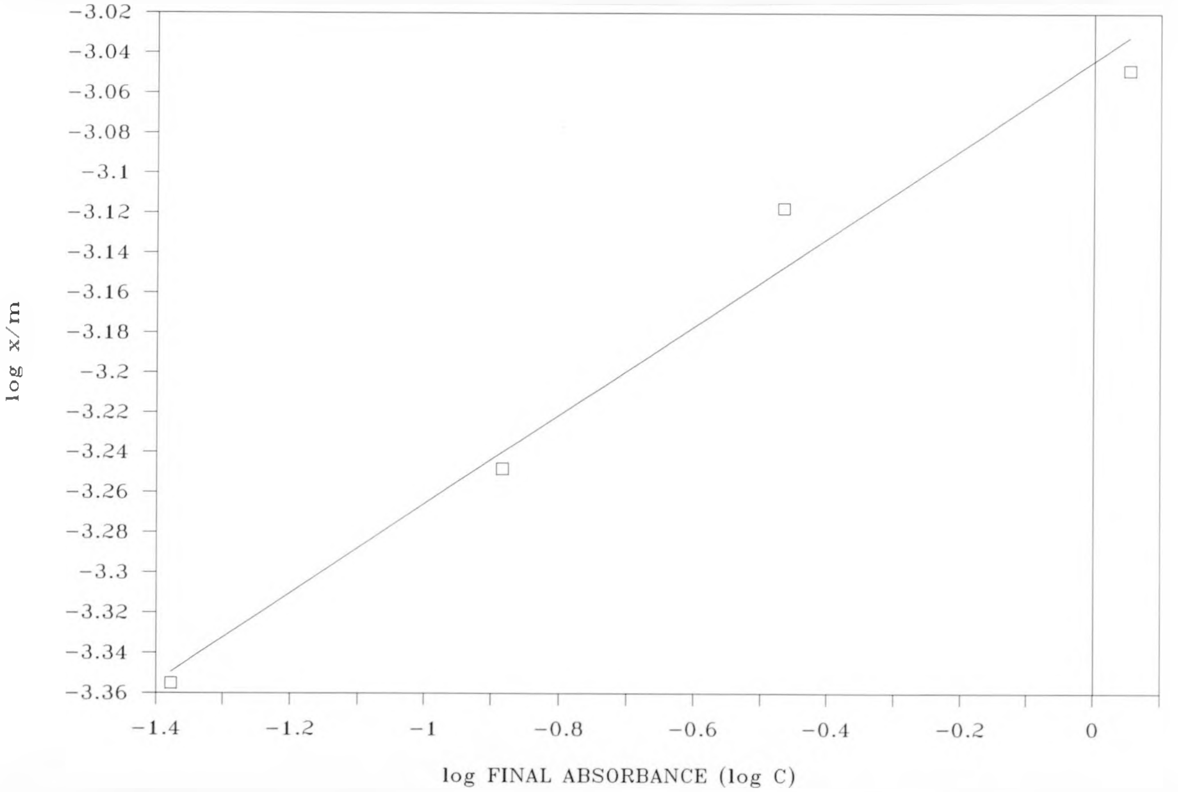

Figure A-12. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using powdered Calgon F-100 activated carbon.

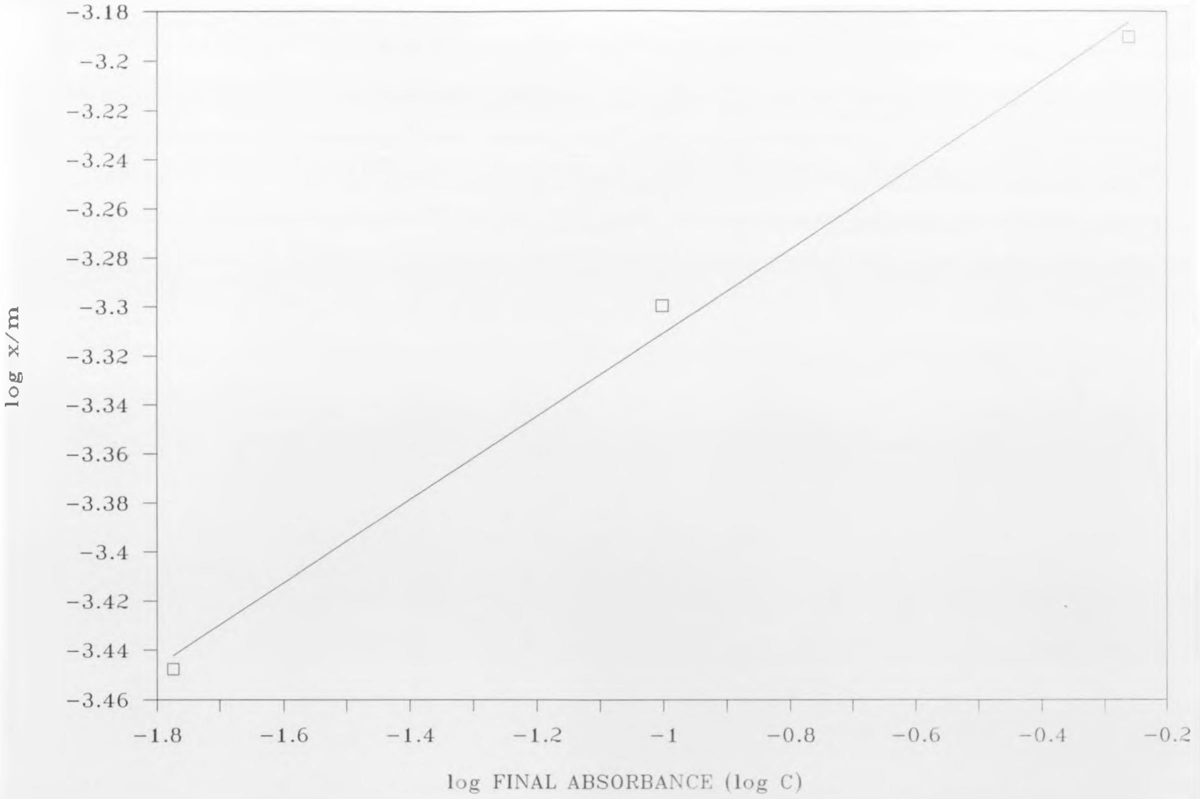

Figure A-13. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using powdered Nuchar S-A activated carbon.

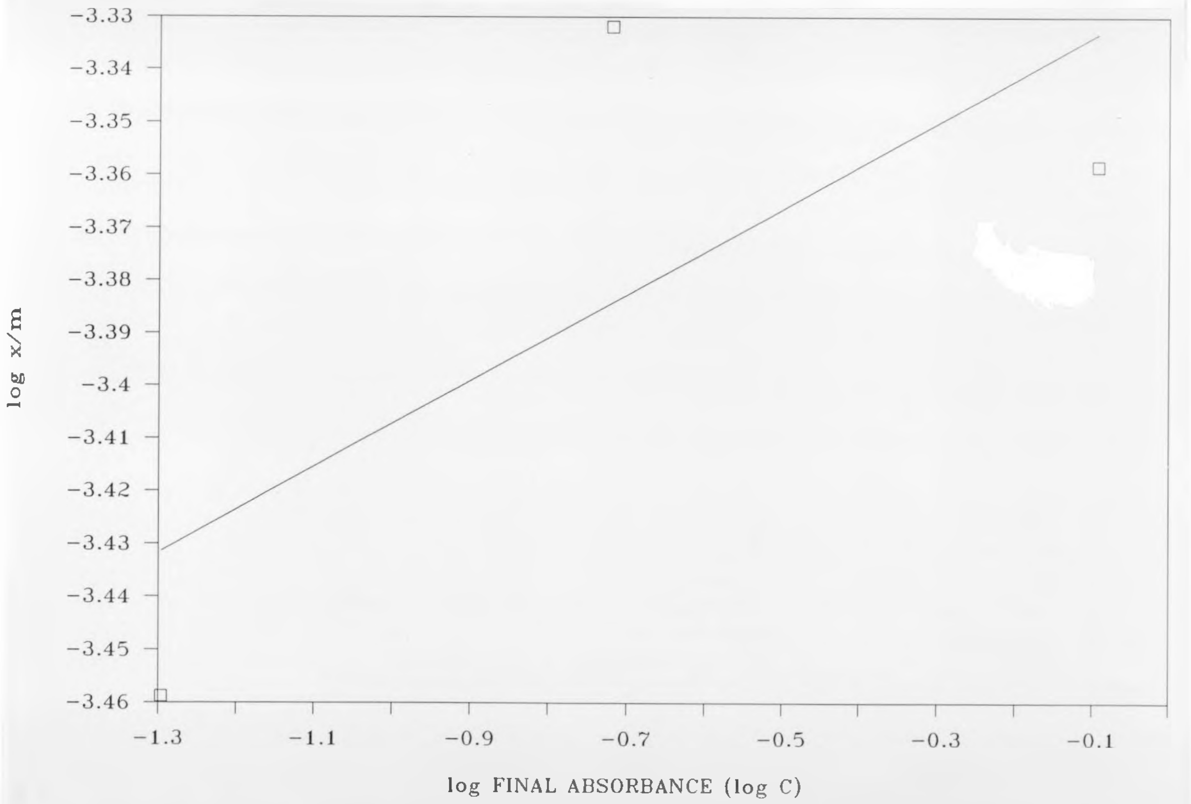

Figure A-14. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using powdered Nuchar S-A activated carbon.

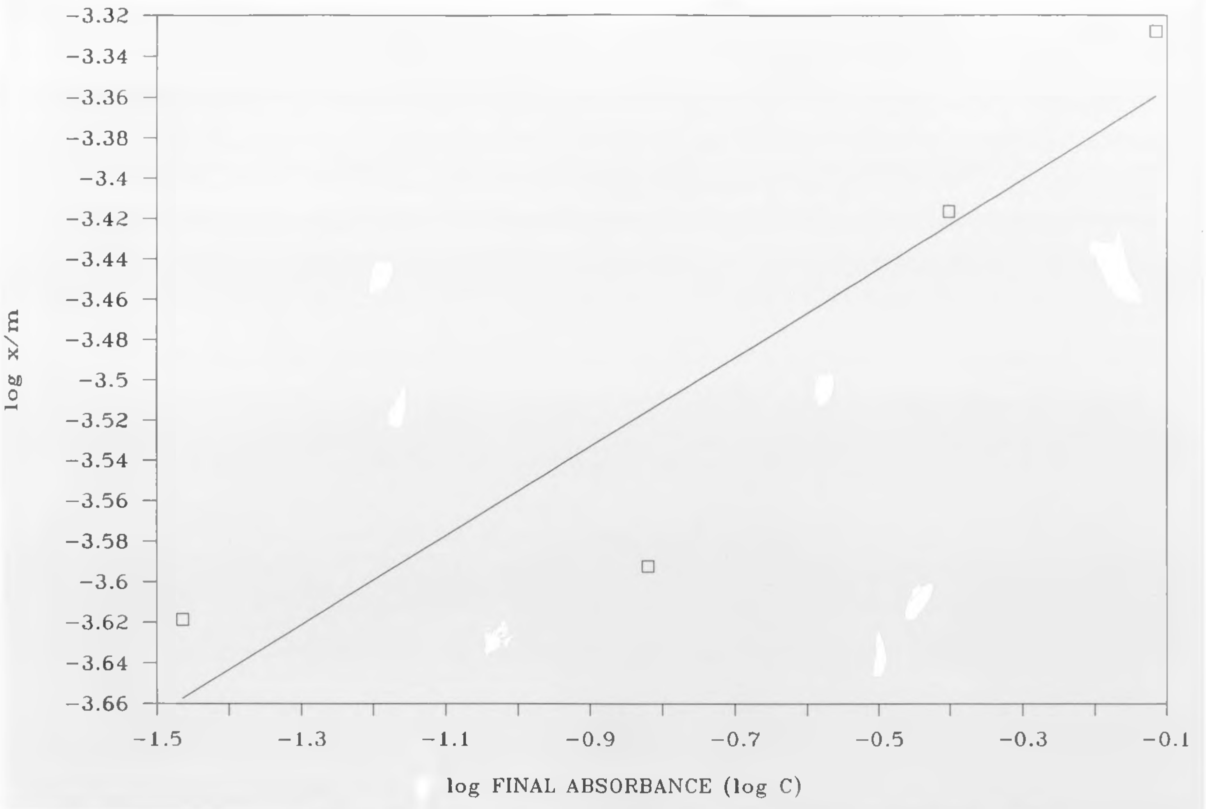

Figure A-15. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using powdered Nuchar S-A activated carbon.

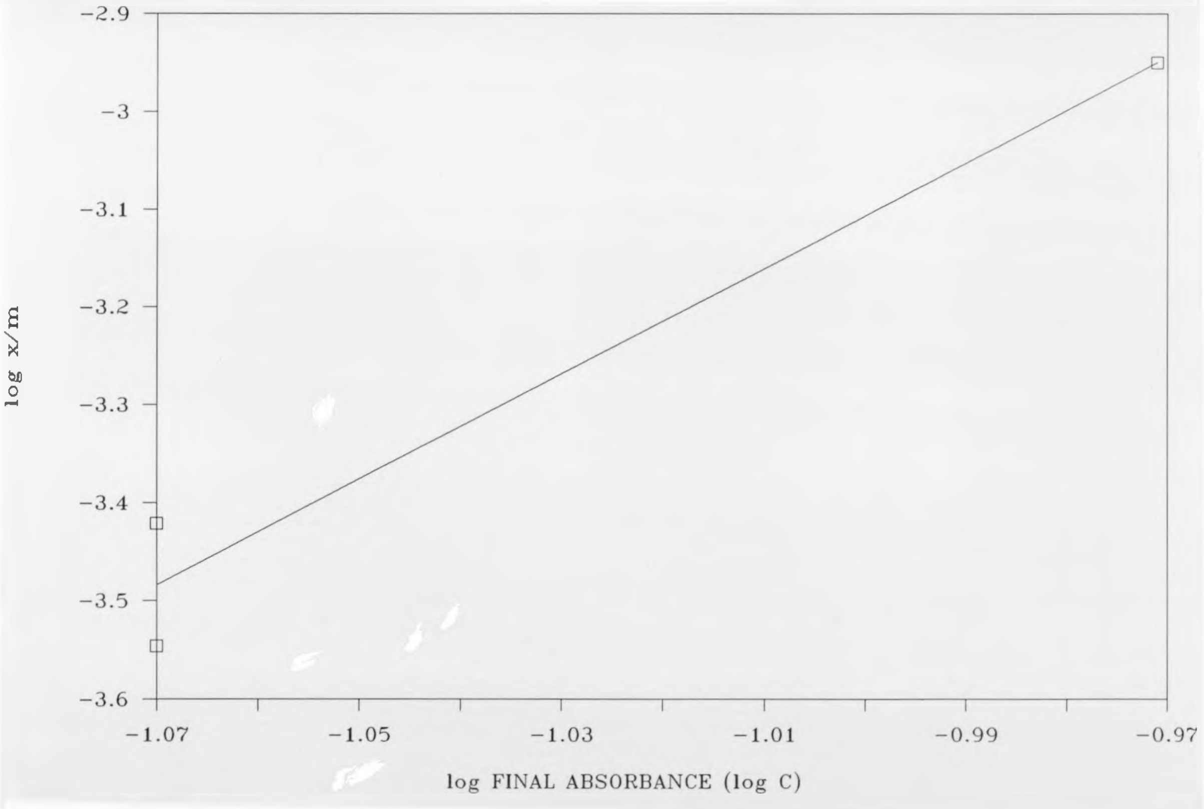

Figure A-16. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using Pleasant Prairie ash.

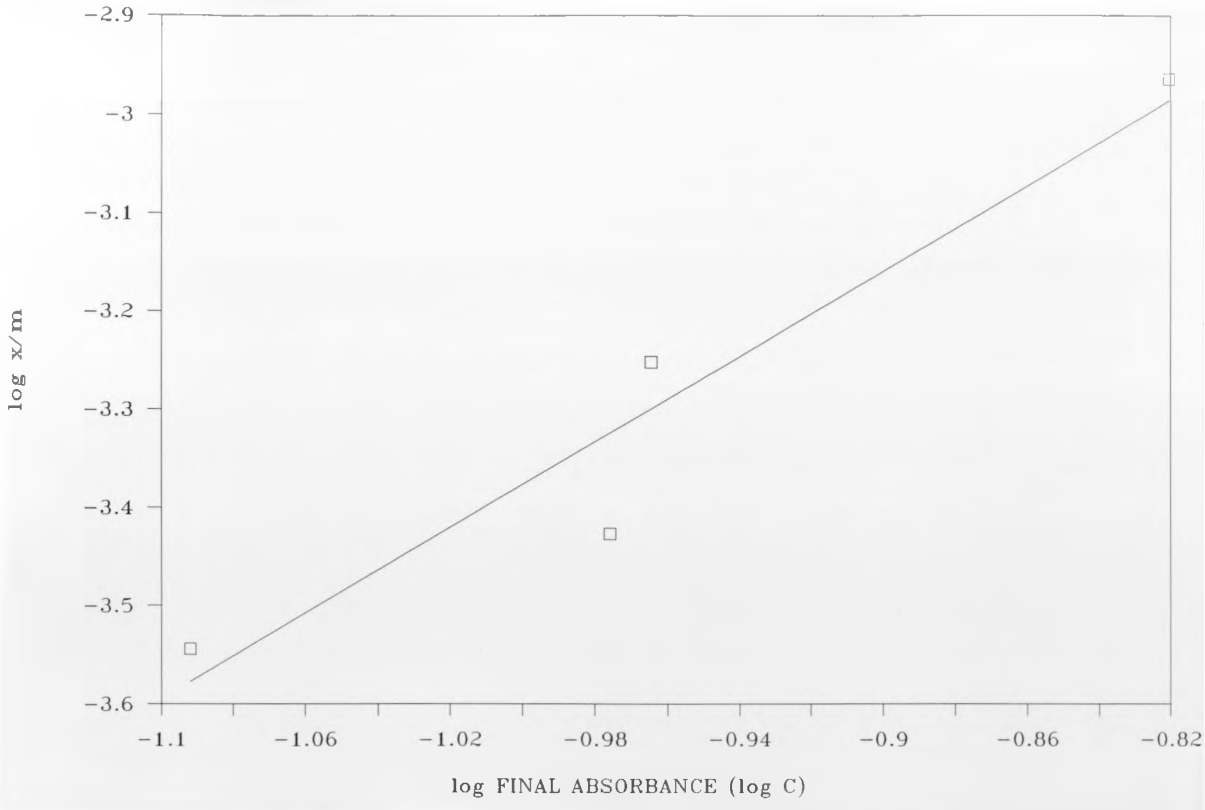

Figure A-17. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using Pleasant Prairie ash.

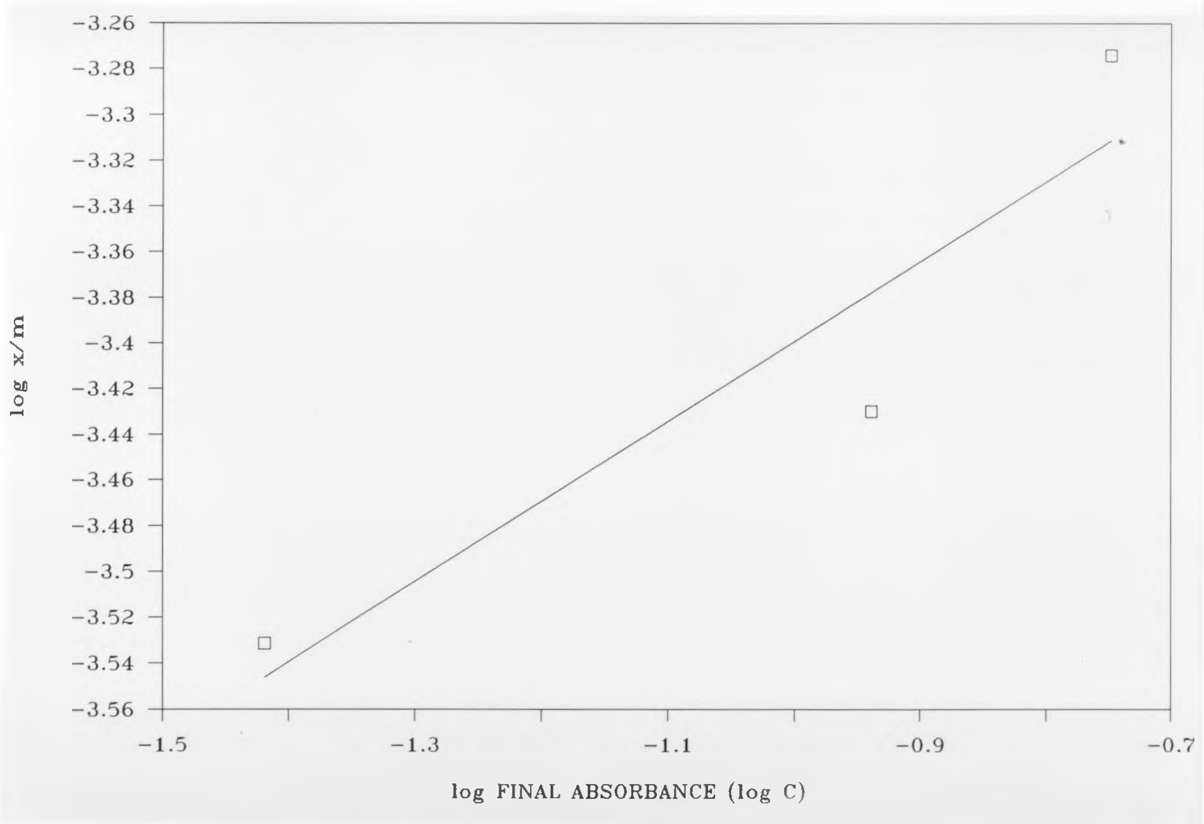

Figure A-18. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using Pleasant Prairie ash.

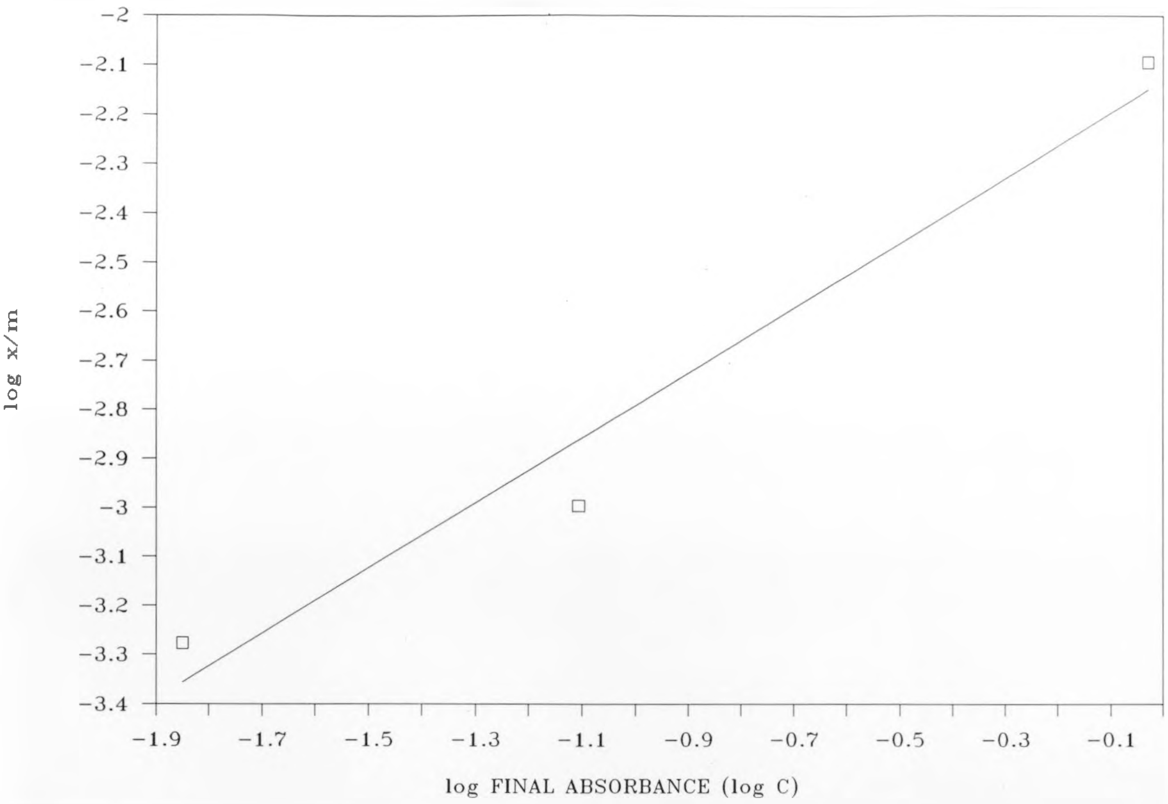

Figure A-19. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using Gentleman Station ash.

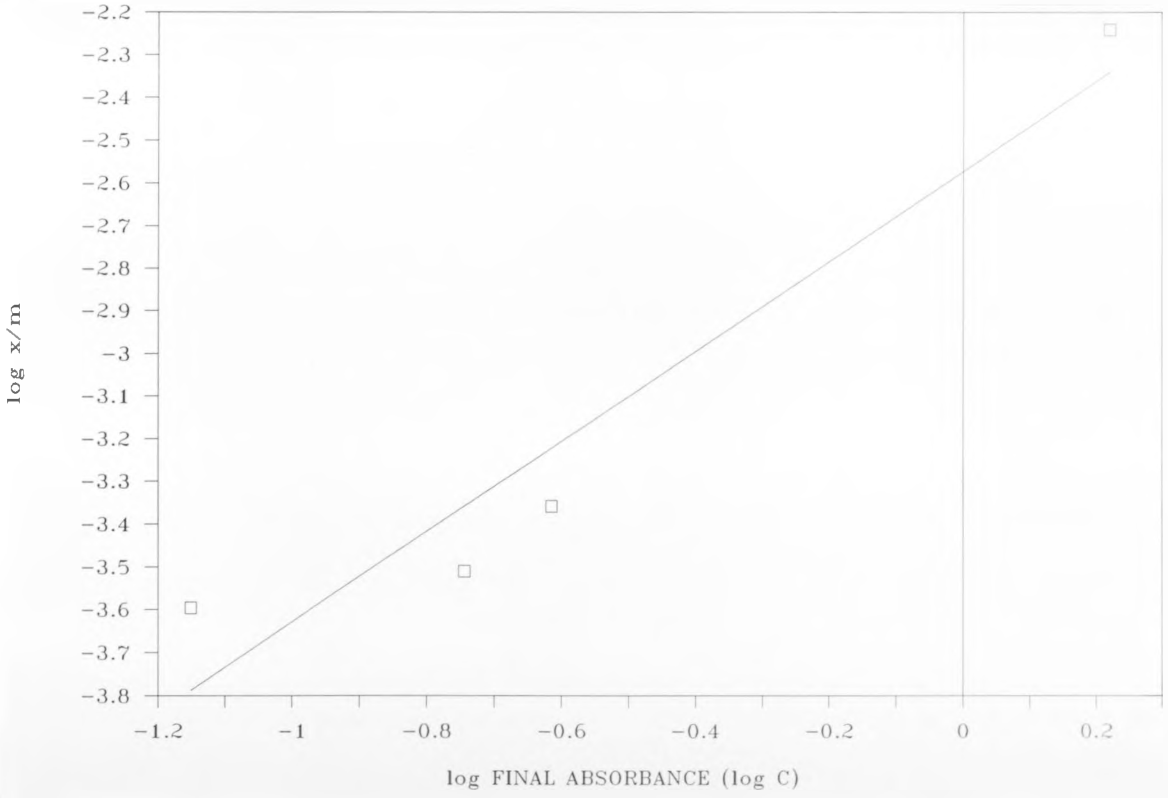

Figure A-20. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using Gentleman Station ash.

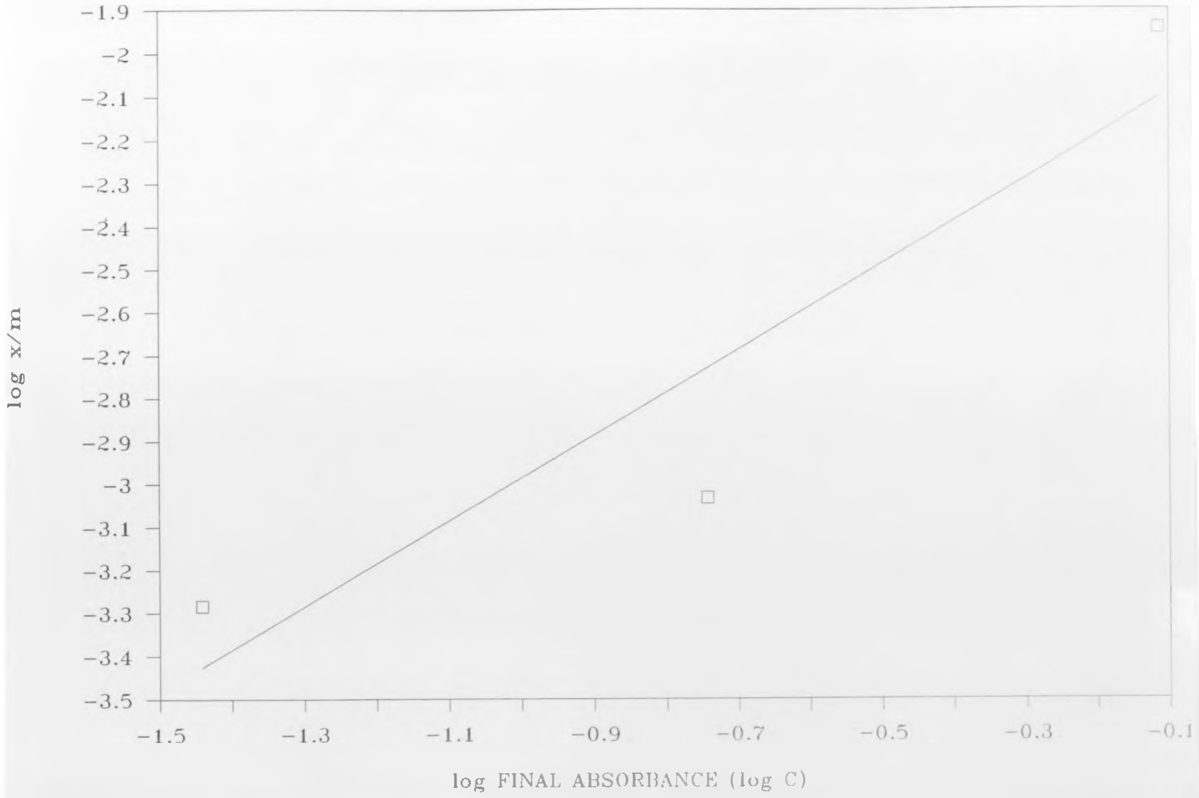

Figure A-21. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using Gentleman Station ash.

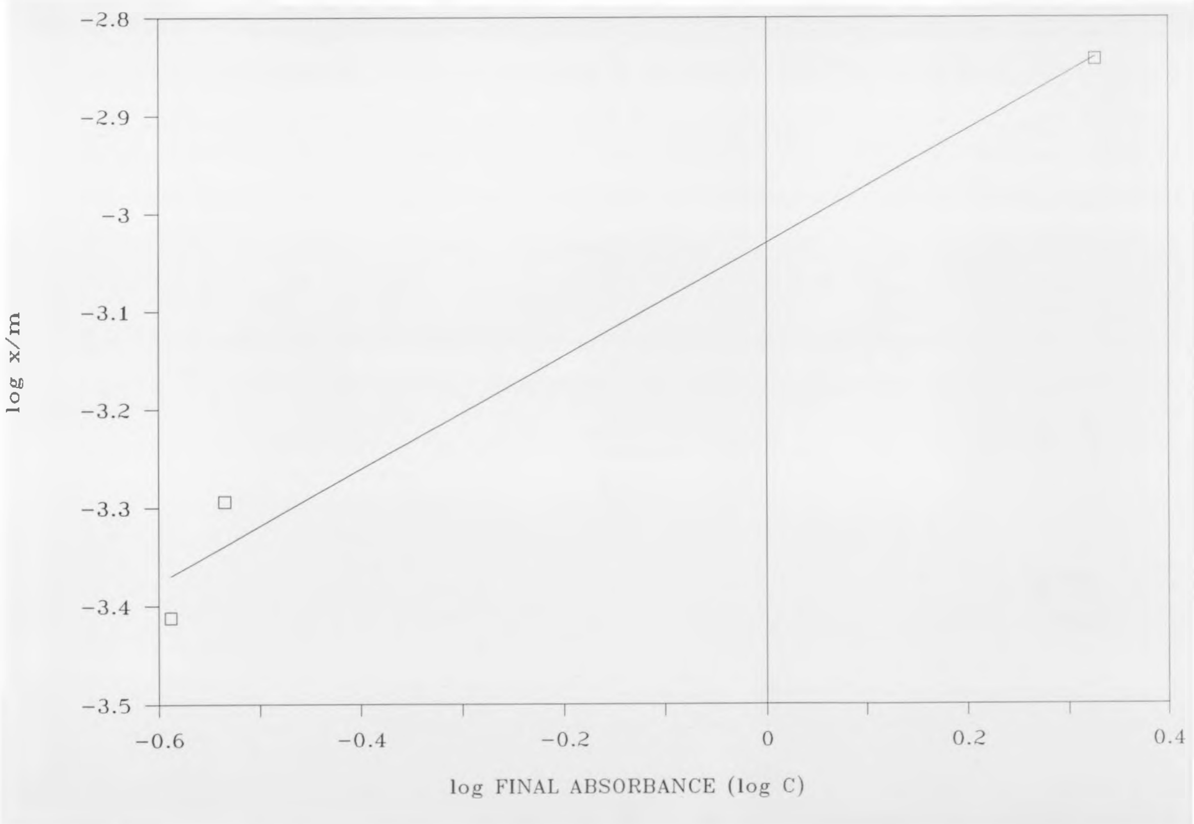

Figure A-22. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using GPGP gasifier ash.

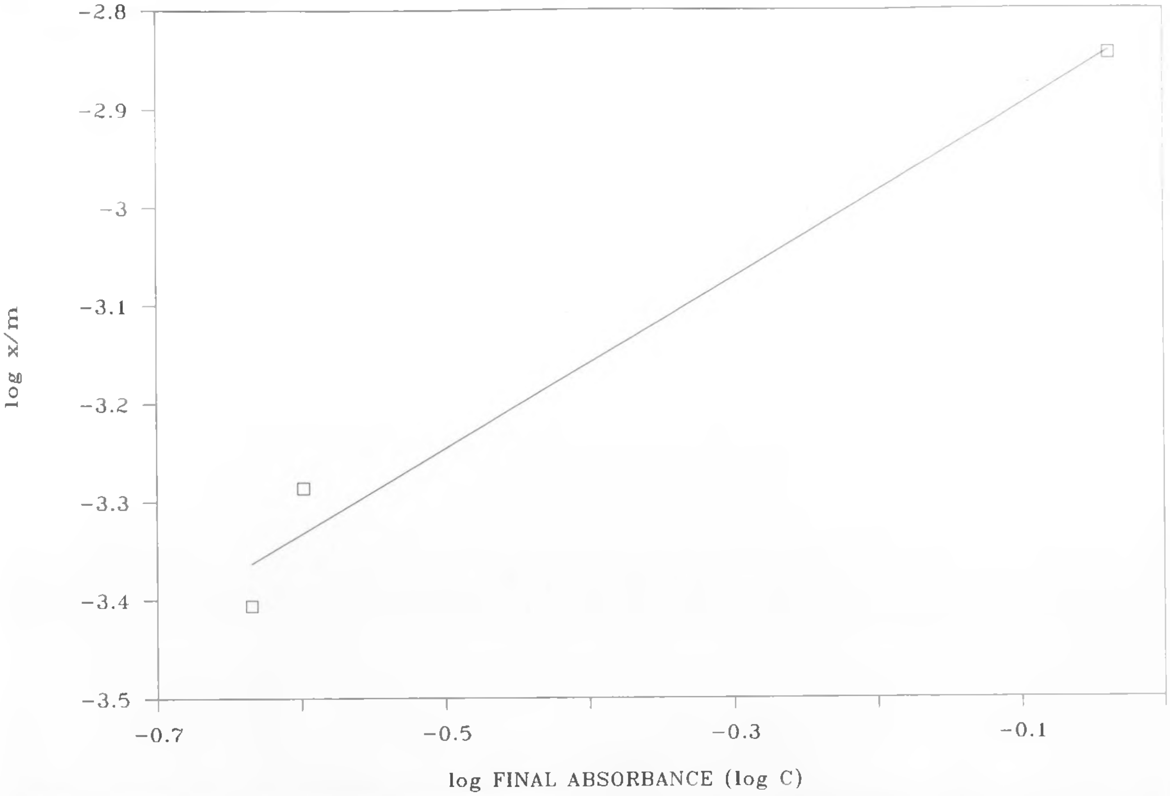

Figure A-23. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using GPGP gasifier ash.

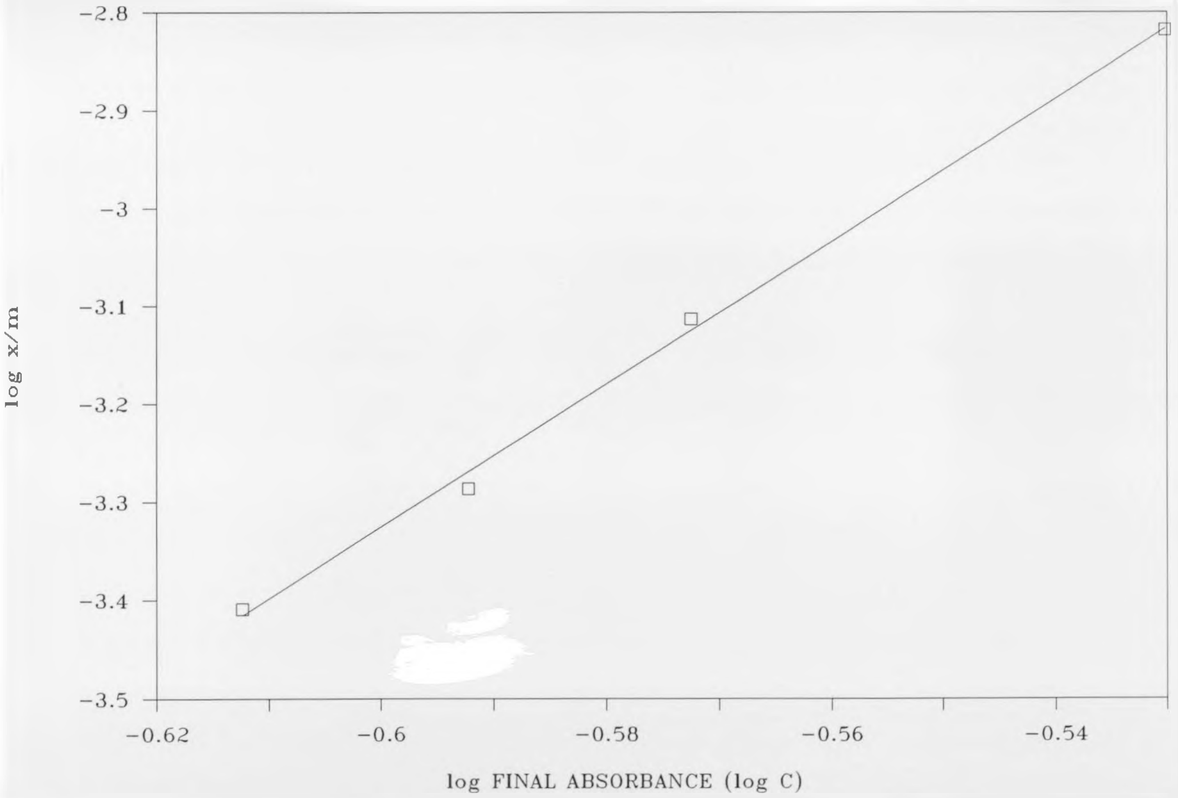

Figure A-24. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using GPGP gasifier ash.

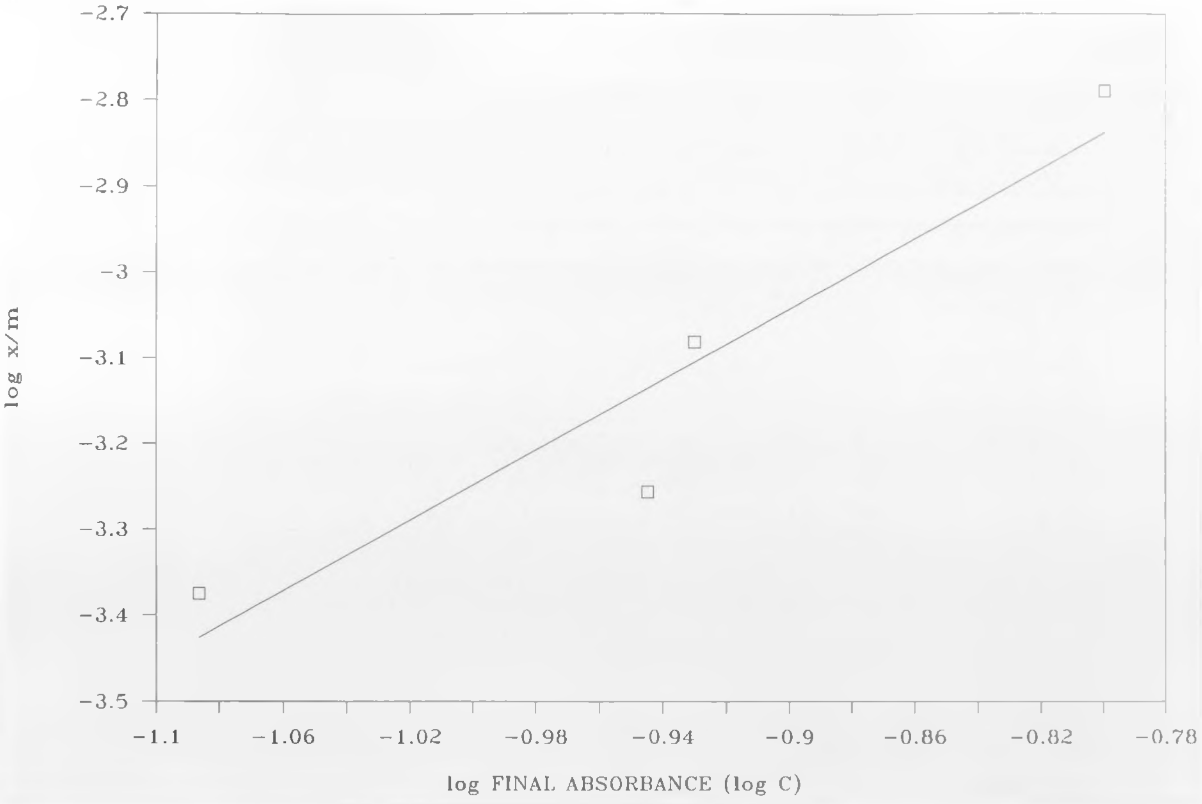

Figure A-25. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using Coal Creek ash.

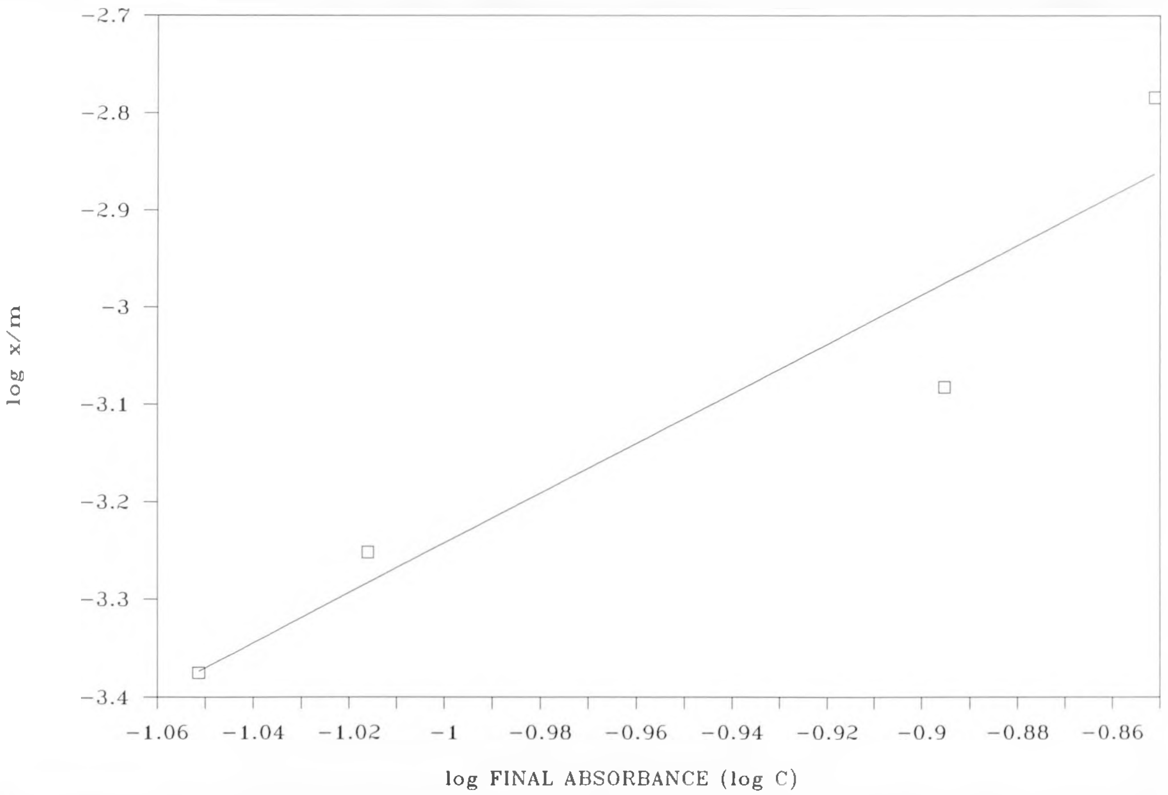

Figure A-26. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using Coal Creek ash.

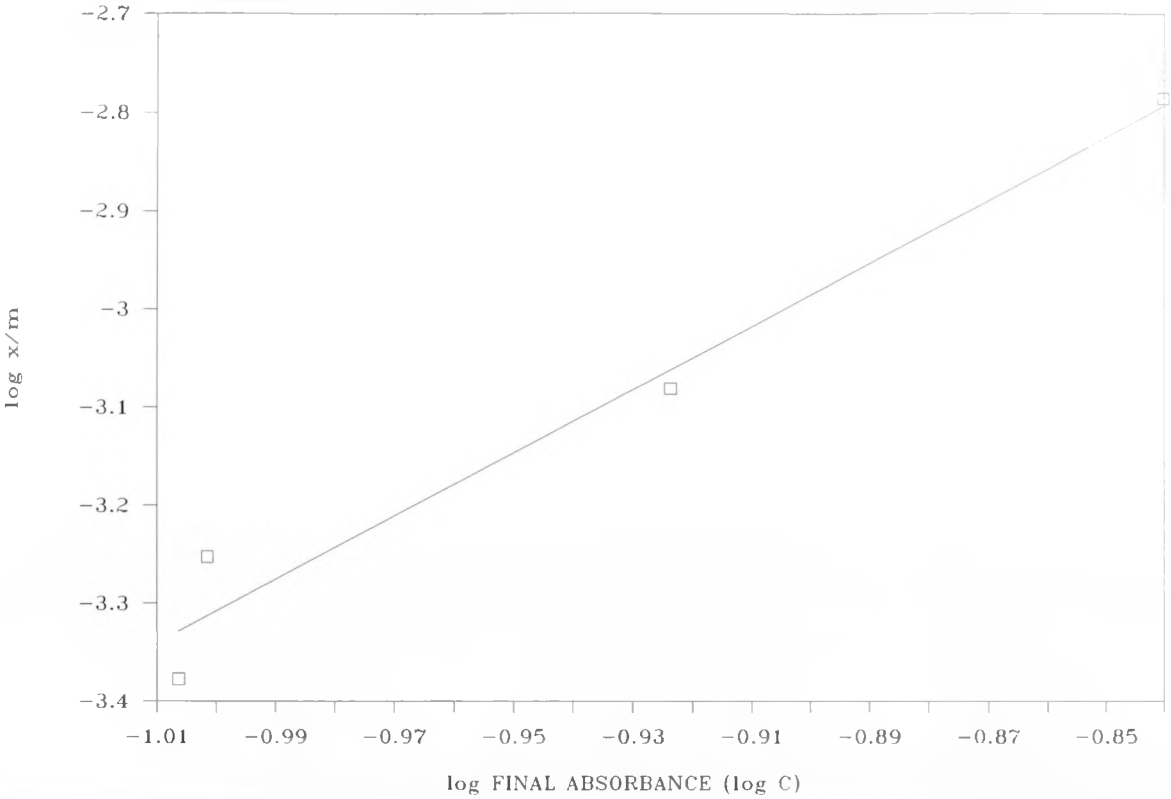

Figure A-27. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using Coal Creek ash.

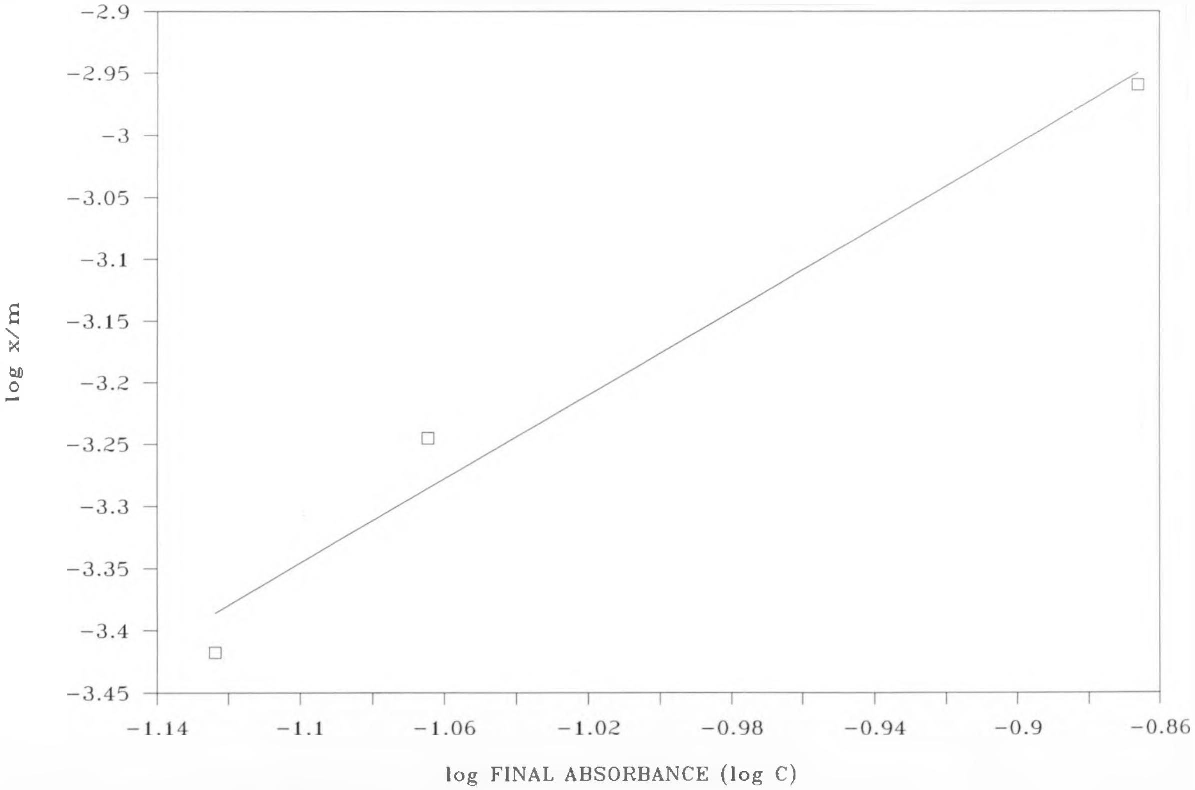

Figure A-28. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 5 using Columbia Portage ash.

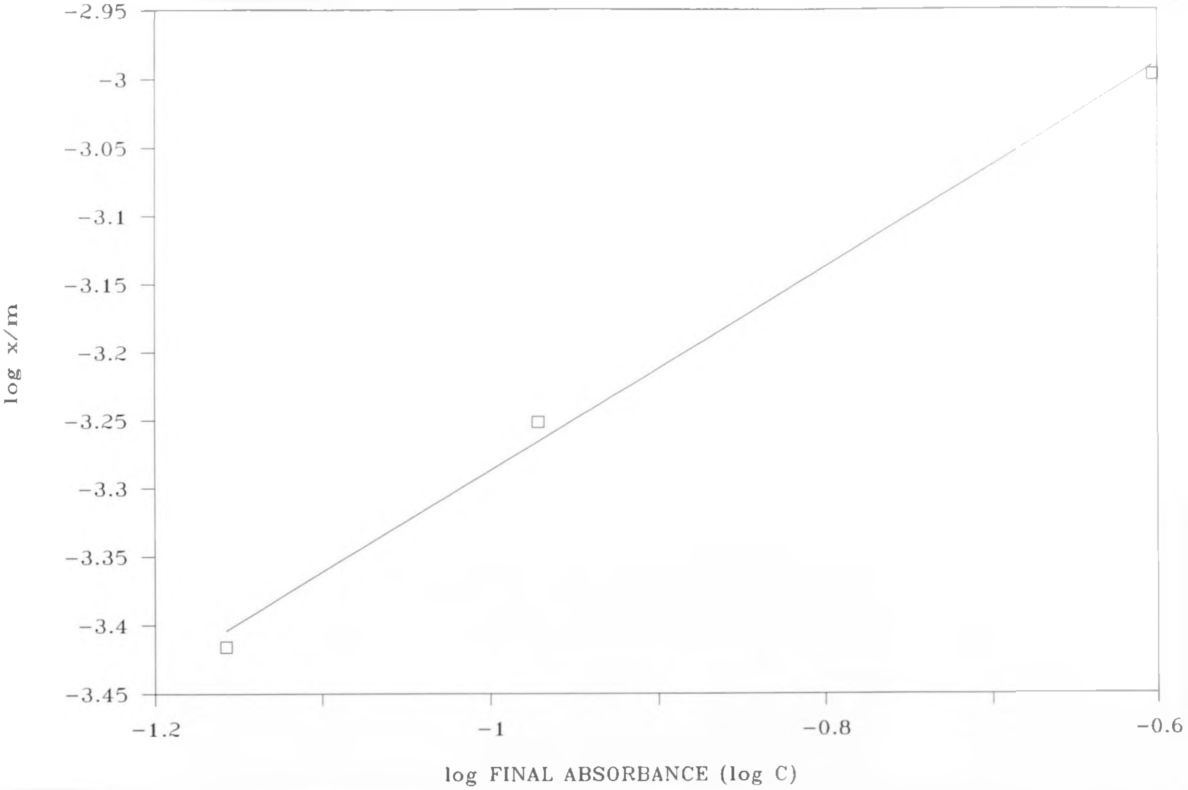

Figure A-29. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 7 using Columbia Portage ash.

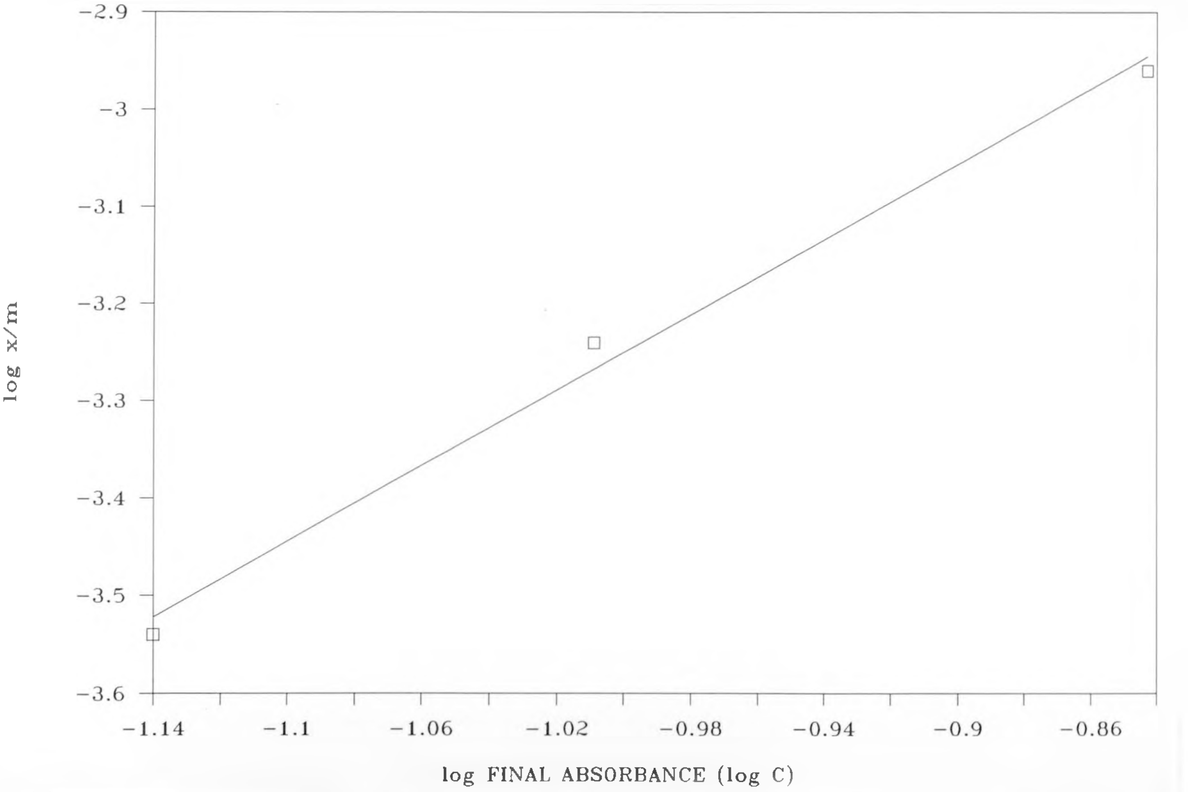

Figure A-30. Freundlich adsorption isotherm for removal of color from GPGP bio-treated stripped gas liquor at a pH of 10 using Columbia Portage ash.

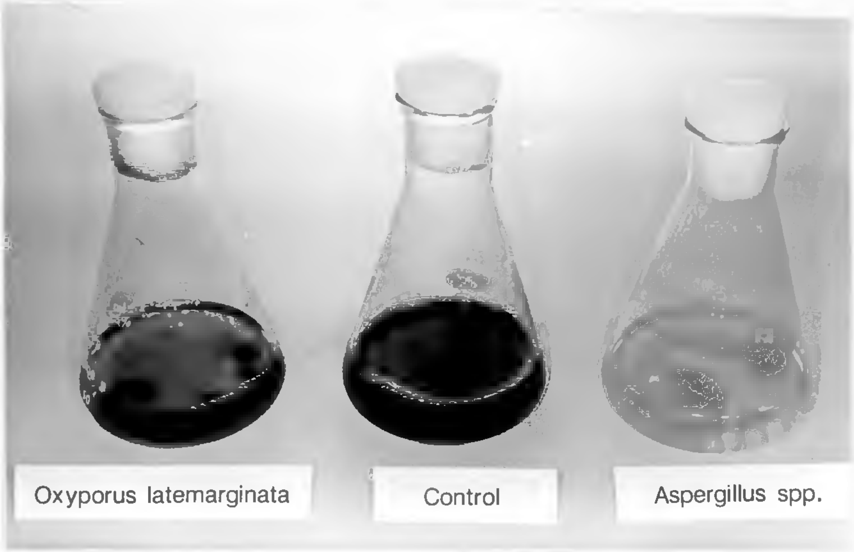

Figure A-31a. Fungal cultures after 10 days of incubation in GPGP bio-treated stripped gas liquor with added dextrose and nutrients.

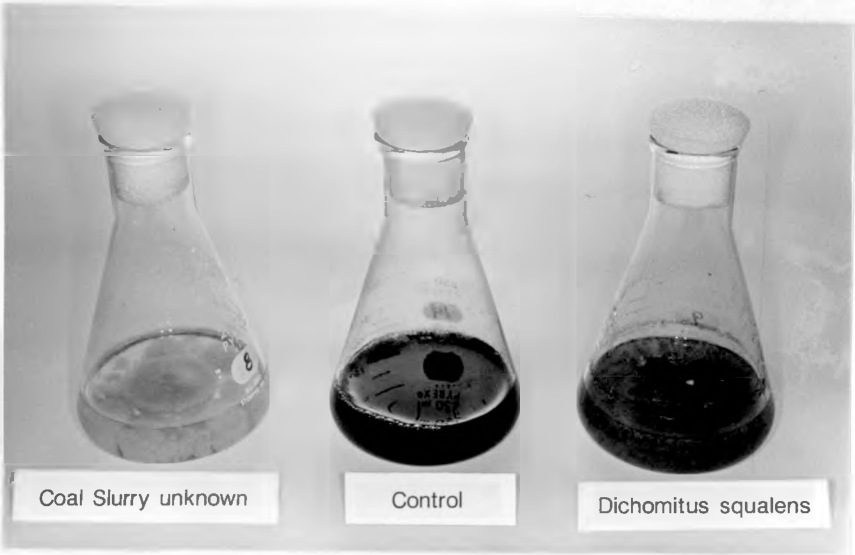

Figure A-31b. Fungal cultures after 10 days of incubation in GPGP bio-treated stripped gas liquor with added dextrose and nutrients.

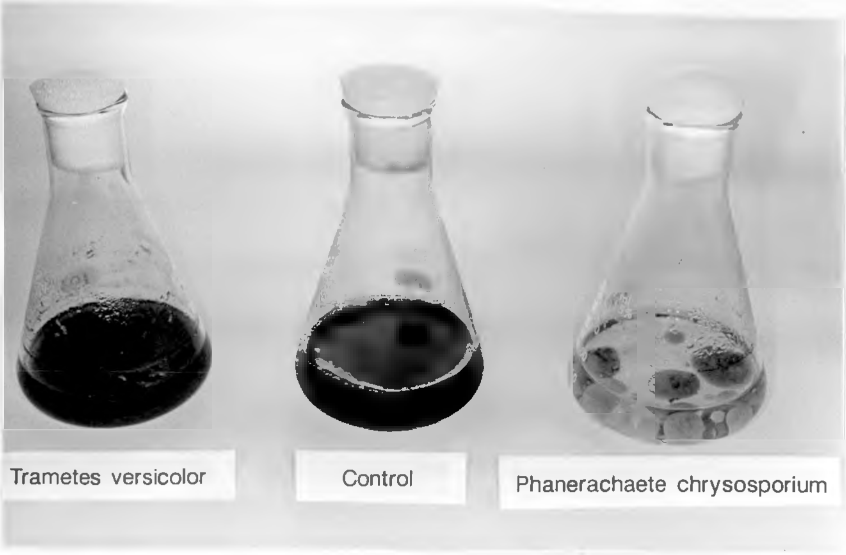

Figure A-31c. Fungal cultures after 10 days of incubation in GPGP bio-treated stripped gas liquor with added dextrose and nutrients.