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# Adsorption of Organic Pollutants onto Natural Adsorbents

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ADSORPTION OF ORGANIC POLLUTANTS ONTO NATURAL ADSORBENTS

By

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In this research, the adsorptive capacities of kenaf, peat moss, hay, and peanut hulls were evaluated for the removal of TNT and 2,4-DCP from aqueous solutions. Adsorbent loading capacities determined by batch studies were verified by continuous column experiments.  It was found that the adsorption capacity of the candidate adsorbents were significantly lower than granular activated carbon (GAC).  The impact of surface modification techniques, such as surface oxidation, were evaluated to study the effect on adsorption capacity.  At lower equilibrium concentrations of the adsorbate (less than 10 ppb), surface oxidation by ozone showed an increase in the adsorption capacity. The same trend was not observed with peroxone and ultrasound pretreatment.  The adsorbent requirement for treating water contaminated with TNT and 2,4-DCP were calculated based on the adsorptive capacity of the adsorbents.  Though the adsorbent requirements for the candidate adsorbents were considerably higher than granular activated carbon, the adsorbent requirement costs for most of the candidate adsorbents

tested were competitive when compared to GAC  costs.

## DEDICATION

I would like to dedicate this thesis to my parents.

## ACKNOWLEDGMENTS

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# CHAPTER I

## INTRODUCTION

Water is used in almost all aspects of human life. About 7 % of the nation's daily water intake is used for industrial purposes (USGS, 1995). Water treatment is becoming one of the more important issues facing industries because of increasingly stringent treatment standards being required by the United States Environmental Protection Agency and pending water shortages. Thus, water treatment poses both technical and economic challenges to industry (Acar and Zappi, 1995). Much of the treatment on-going within industry is focused toward treating water contaminated with organic pollutants, because organics are common waste constituents. Technologies, such as biotreatment, air stripping, chemical oxidation, and granular activated carbon (GAC) adsorption, have been used with some success (LaGrega *et al.,* 1994).

The biological treatment of organics involves the removal of organic matter by microorganisms (LaGrega *et al*., 1994). Conventional biotreatment is the most popular industrial wastewater treatment process utilized within the United States. Biological treatment of many organic chemicals can be accomplished if proper microbial communities are established, maintained, and controlled. However, when the influents do not contain sufficient levels of organic substrates, biological treatment units cannot be supported.

Additionally, many organic compounds cannot be easily biodegraded (Zappi *et al.*, 1993).

Air stripping is a phase-change process that involves the volatilization of compounds by contacting polluted water with air to facilitate the transfer of water-borne pollutants into the air phase (LaGrega *et al.,* 1994). When the contaminant has a low Henry's Law Constant, air stripping cannot be used (Haas and Vamos, 1995). Also, recent regulatory guidance requires treatment of air exiting air stripper units due to concerns over air pollution; thereby, increasing cost and operations complexity.

Chemical oxidation processes use powerful chemical oxidizers to destroy organic contaminants within contaminated waters and to remove pathogens from drinking water sources (Ho and Daw, 1988). Ozone, chlorine, hydrogen peroxide, and potassium permanganate are typical oxidizers used in chemical oxidation processes (Zappi, 1998). These processes are most economical when organics are present at low concentrations, since the oxidizing agents are nonspecific and react with any reducing agent (pollutant) in the water to be treated (LaGrega *et al*., 1994). Chemical oxidation is often considered a viable alternative water treatment process, but the technology is still developing, sometimes costly, and requires highly trained operators (Langlais *et al.,* 1991). Plus, the presence of hydroxyl radical scavengers within the influents and poor influent UV transmissivity can adversely impact performance (Zappi, 1995).

Adsorption is a physical treatment process where the pollutants (the adsorbate) physically adsorb onto the surface of the adsorbent via weak electrostatic forces of attraction. Granular activated carbon (GAC) is the most commonly used adsorbent for

the removal of organic compounds from groundwater and industrial waste streams. Although carbon adsorption is a well-developed technology that is widely utilized in drinking water systems as well as for pollution control, GAC use has drawbacks, which include:

    a.   The cost of activated carbon (approximately $2.00/lb).

    b.   Activated carbon is usually loaded into and out of the adsorbers using water-carbon slurries, which increases system complexity and cost.

    c.   Activated carbon is easily crushed into useless fines during handling and under high impact and overburden stresses.

    d.   The spent activated carbon typically has to be transported to a different site to be either regenerated or disposed off, which increases operating costs.

Due to the above listed drawbacks, the potential exists for replacing GAC with innovative, yet cost effective natural adsorbents. This potential has instigated considerable research focusing on the use of natural adsorbents for adsorption (Pollard *et al.*, 1992; Kim *et al.*, 1997; Srivastava *et al.*, 1997). The candidate adsorbents tested in this research were kenaf, peat moss, hay, and peanut hulls.

CHAPTER II

RESEARCH HYPOTHESIS AND GOALS

In this research, we propose to use natural adsorbents instead of GAC and replace the regeneration step by making use of a compost pile. Composting the spent adsorbent will not only degrade the adsorbent material, but also the adsorbate (Zappi *et al.*, 2000). Thus, severe drawbacks involved in off-site regeneration of the spent activated carbon and operating costs can be considerably reduced. A conceptual process flow path of the proposed system is shown in Figure 2.1.

The specific purpose of this research was to assess the potential of several candidate natural adsorbents in adsorbing organic pollutants from aqueous solutions and the evaluation of these adsorbents within saturated column reactors under dynamic operational flows. Another study was on-going at the time of the drafting of this thesis and is focusing on the composting step. This study is being performed by Gaya Ekanayake under the direction of Dr. Mark E. Zappi.

Potential advantages of the proposed process include:

a. The natural adsorbent-based biosorptive process is expected to be much cheaper than activated carbon in that adsorbents are a renewable resource that are cheaply cultured within the Southeastern United States (Zappi *et al.*, 2000; Brown *et al.*, 2000).

The cost of the candidate adsorbents used in this study were generally less than $0.20 per pound.

b. The adsorbents are easily prepared using processing techniques that economically wash, crush and segregate the various fractions (Zappi *et al*., 2000).

c. The adsorbents are easily stored and are extremely stable under high impact and overburden stresses (Zappi *et al.,* 2000).

The specific objectives of this study were to:

a. Evaluate the adsorptive capacity of the candidate natural adsorbents for removal of the test adsorbates from aqueous solutions.

b. Verify the loading capacities determined by batch testing through performance of columns operated under variable operating conditions.

c. Evaluate the impact of adsorbent modification techniques, such as surface oxidation, on the adsorptive capacity of the candidate adsorbents.

Effluent

Spent Adsorbent to Compost

Compost pile

Fresh Adsorbent into Column

Influent
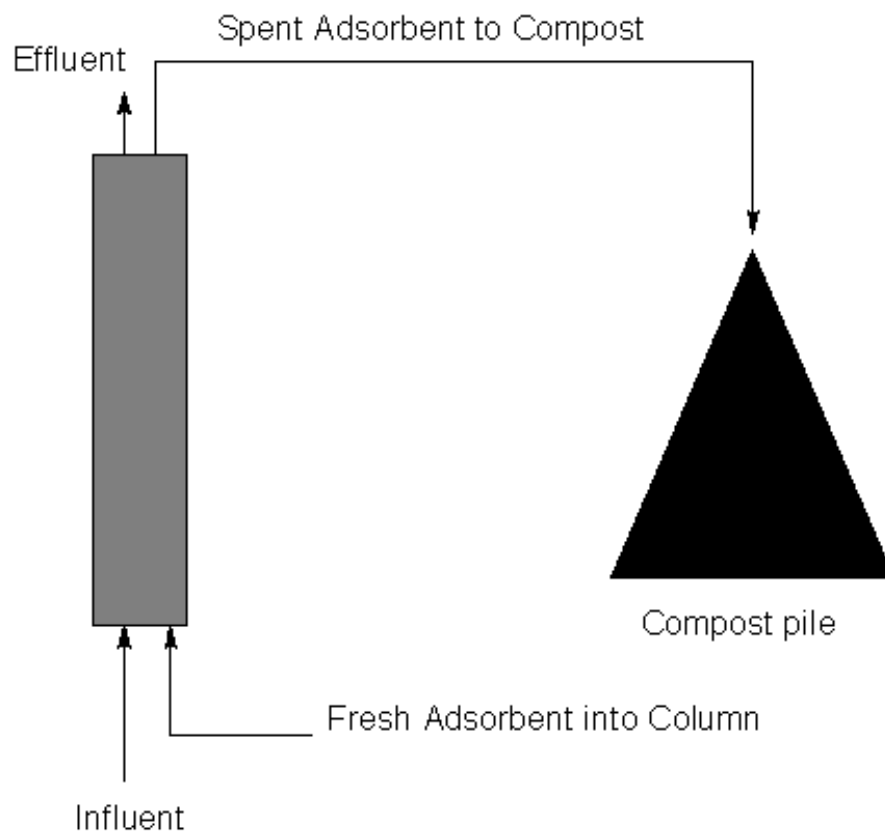
Figure 2.1. Conceptual process flow path.

# CHAPTER III

## ADSORPTION BASICS

Adsorption is a process in which a soluble chemical (the adsorbate) is removed from a fluid by contact with a solid surface (the adsorbent).  It is used in industry for product separation and waste treatment.  Adsorption is actually a mechanism in which the forces of interaction between surface atoms and the adsorbate molecules are similar to Van der Waals forces that exist between all adjacent molecules (LaGrega *et al*., 1994). There are both attractive forces and repulsive forces with the net force depending on the distance between the surface of the adsorbent and the adsorbate molecule (Cooney, 1999). In general, adsorption is the process by which a component moves from one phase to another while crossing some boundary.  Experiments by several scientists including Brunauer, Emmett and Teller (Brunauer *et al*., 1938), McBain (McBain, 1935), and Langmuir (Langmuir, 1918) focused on the manner in which adsorbents removed adsorbates from both  gases and liquids.  As a result of these important studies, quantitative theories on adsorption have emerged.  It was found that the observed effect of adsorption was achieved within porous solids and that adsorption was the result of interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase (Crittenden and Thomas, 1998).

When there is a lack of electron symmetry around the nucleus, a dipole moment is created. The electron distribution may be symmetrical on a time-averaged basis, but at any instant of time it is not, leading to transient dipole moments. The dipole moment of an adsorbate molecule induces a dipole moment on the surface atom or molecule and the interaction of these two dipole moments causes a transient attractive force to exist (Cooney, 1999). These attractive forces were called by London (1930) as dispersion, in that they have a similarity to optical dispersion phenomena.

The attractive forces are related to the distance of separation by a factor r, which is the distance between a surface molecule and an adsorbate molecule (Cooney, 1999). The dipole-dipole force is inversely proportional to the sixth power of r. Depending on the nature of the molecules, there could be dipole-quadrapole interactions and quadrapole-quadrapole interactions. The dipole-quadrapole and quadrapole-quadrapole interaction forces fall off as $1/r^8$ and $1/r^{10}$, respectively. Thus, they are much weaker than dipole-dipole forces (Cooney, 1999).

Repulsive forces develop when the electron cloud of the adsorbate molecule overlaps with the surface molecule (Cooney, 1999). The repulsive force increases in proportion to $1/r^{12}$, which means that the repulsive forces increase rapidly as the distance shortens.

The combined effects of the attractive and repulsive forces is expressed by the Lennard-Jones "6-12" Potential Function (Lennard-Jones, 1928, 1932), which is presented below:

$$\Phi = 4 \in [(\sigma/r)^{12} - (\sigma/r)^6] \qquad\qquad (3.1)$$

where,

$\Phi$ = potential function.

s = collision diameter, the distance of separation for which the force of interaction
is zero

$\in$ = depth of the potential well.

Adsorption can be classified as either physical or chemical. Physical adsorption involves weak forces, and is, therefore, reversible. Physical adsorption occurs at low temperatures. Physical adsorption is very similar to a condensation process, and thus, it is exothermic with a heat of adsorption similar to that of the latent heat of condensation (Cooney, 1999).

Chemical adsorption or chemisorption is important in gas-phase catalysis, but is not generally relevant to liquid-solid adsorption at ordinary temperatures (Cooney, 1999). Chemisorption occurs at high temperatures with a significant activation energy, which involves strong bonds and is not reversible. The heat of adsorption is typically high in chemisorption and is similar to heat generated during a chemical reaction.

There are several factors that impacts physical adsorption (LaGrega *et al.*, 1994; Cooney, 1999). The major factors which affect physical adsorption include the surface area of the adsorbent, pore structure of the adsorbent, surface chemistry of the adsorbent, nature of the adsorbate, pH of the solution, and the presence of competing adsorbates. It is due to these factors, physical adsorption is considered to be a complex phenomena.

Surface area of the adsorbent is one of the most important factors on which adsorption greatly depends. The surface area is comprised of two types, the external

surface area and the internal surface area (pore walls).  The external surface of the

adsorbent contributes to the external superficial surface area.  The pores of the adsorbent

contribute largely to the internal surface area.  Since physical adsorption greatly depends

upon the surface area, the greater the surface area of the adsorbent, the greater the

capacity for adsorption (Cooney, 1999).

The pore structure of the adsorbent material is almost as important as the surface

area.  The pore diameter for most media  ranges from less than 10 to over 100,000

Angstroms (Hassler, 1963).  The pore structure should be such that the adsorbate

molecule enter the pores and adsorb onto the inner surface of the pores.  If the adsorbate

molecules are larger than the pore diameter, lesser adsorption would take place because

of stearic hindrances.

The surface of an adsorbent is typically composed of various surface functional

groups (SFG).  Adsorption of organic adsorbates is greatly dependent on the amount and

nature of surface oxide groups (Cooney, 1999).  Surface functional groups

(carbon/oxygen) are created by oxidation occuring during the activation process of an

adsorbent.  Some of the common basic functional groups created are lactones, quinones,

and carboxylates (Ishizaki and Marti, 1981).  Some of the common acidic functional

groups created are phenolic, hydroxyl, carbonyl, and carboxylic acids (Corapcioglu and

Huang, 1987).  It has been found that the presence of acidic functional groups on the

surface of the activated carbons impact the ability of the adsorbent to adsorb phenolic

compounds under oxic conditions.  The presence of oxygen-containing basic groups such

as chromene-type and pyrone-type are a key factor in promoting irreversible adsorption (Vidic *et al.*, 1993).

Strongly dissociated adsorbates are weakly adsorbed when compared to nondissociated adsorbates (Cooney, 1999). The more nonpolar an adsorbate, the higher the adsorption capacity. This is attributed to the fact these adsorbate molecules tend to prefer the adsorbent surface rather than being in the solution (Cooney, 1999). It has also been shown that an increase in the molecular weight of the adsorbate will generally enhance adsorption until the size of the adsorbate is larger than the pore size of the adsorbent. Typically, aromatic compounds are more adsorbable than aliphatic compounds of similar molecular size and branched-chain molecules are generally more adsorbable than straight-chain molecules (Cooney, 1999). Double and triple carbon bond organics tend to adsorb better than single carbon bond organics (LaGrega *et al.*, 1994). In addition, solubility of the adsorbate is also an important factor. In general, the lower the solubility of the adsorbate, the higher the adsorption capacity since the forces of attraction between the adsorbate molecules and the adsorbent surface molecules will be greater than the forces of attraction between the adsorbate and the solvent molecules.

The pH of the solution is a major factor in determining adsorption. Generally, acidic species adsorb better at low pH, while basic species adsorb better at higher pH. Ward and Getzen (1970) found that maximum adsorption occurs at a point where pH = pKa for each adsorbate.

The presence of competing adsorbate increases the competition for available adsorption sites. In general, the presence of competing adsorbates will reduce the adsorption capacity of all adsorbates onto the adsorbent (Cooney, 1999).

Adsorption occurs when an adsorbent comes in contact with a liquid containing the adsorbate and adsorption sites on the adsorbent become filled. Equilibrium occurs when the adsorption sites are filled. Equilibrium is a phenomenon when the rate of adsorption and the rate of desorption are equal (Cooney, 1999). This is also the case when the effluent exiting an adsorption column contains pollutants at greater concentrations than is allowed. With a column system the adsorbent is said to be "spent."

The relationship between the amount of adsorbate adsorbed onto the adsorbent surface and the equilibrium concentration of the adsorbate in solvent at equilibrium at a constant temperature may be estimated by various adsorption isotherm models.

## **Overview of Adsorption Models**

Freundlich Isotherm Model : The Freundlich model is by far the most utilized isotherm model in wastewater treatment. It has been reported that data for the adsorption involving adsorbates within a liquid phase is best fitted using the Freundlich model (Cooney, 1999). The Two-Parameter Freundlich model relates the sorbed phase concentration to an equilibrium concentration of the adsorbate according to the following

equation:

$$\frac{X}{M} = kC_f^{1/n}$$  (3.2)

where,

X= Mass of solute adsorbed (mg)

M= Mass of adsorbent (g)

$C_f$ = Final aqueous phase concentration (mg/l)

k, n = Empirical constants

The value for the constant k is typically reported at water phase equilibrium concentration of 1 mg/l (i.e., $C_f$ = 1), when the equation is transformed to the form "X/M = k", and thus, k (adsorptive capacity) has the units of w/w or as mg/g for the example stated.

The Freundlich model implies that the energy distribution for the adsorption sites is exponential in nature (Cooney, 1999). The rates of adsorption and desorption vary with the adsorption energy of the sites and there is a possibility for more than one monomolecular layer of adsorptive coverage. The Freundlich model also does not require that the surface coverage must approach a constant value corresponding to one complete monolayer, as $C_f$ gets larger. At high concentrations, the equation would fail to fit experimental (Cooney, 1999).

Langmuir Isotherm Model: The Two Parameter Langmuir model has the following form:

$$\frac{X}{M} = \frac{bq_mC_f}{1 + bC_f}$$

(3.3)

where,

X = Mass of solute adsorbed (mg)

M = Mass of adsorbent (g)

$C_f$ = Final aqueous phase concentration (mg/l)

The parameter $q_m$ (mg/g) is the maximum value that X/M can achieve as $C_f$ becomes larger. Physically, it represents the concentration of the adsorbate on the surface when one complete monomolecular layer of coverage is achieved and b (l/mg) is the second parameter (Langmuir, 1918). The Langmuir Model generally is a better model for the adsorption of gases onto solids, whereas, the Freundlich Model is a better model for the adsorption of liquid solutions (Cooney, 1999).

Langmuir-Freundlich Isotherm Model: This is a three-parameter isotherm model given by:

$$\frac{X}{M} = \frac{b \; q_m \; C_f^{1/n}}{1 + b \; C_f^{1/n}}$$

(3.4)

where,

X = Mass of solute adsorbed (mg)

M = Mass of adsorbent (g)

$C_f$ = Final aqueous phase concentration (mg/l)

$q_m$ (mg/g), b (l/mg), and n are the three constants.  The equation is also known as the

Sips Equation.  It has been primarily used for aqueous benzene and toluene adsorption

subject to granular activated carbon systems (Hindarso *et al.*, 2001).


Radke and Prausnitz Model: Radke and Prausnitz (1972) proposed a three-parameter

isotherm model given by:


$$\frac{M}{X} = \frac{1}{aC_f} + \frac{1}{bC_f^{\beta}}$$ (3.5)


where,

X = Mass of solute adsorbed (mg)

M = Mass of adsorbent (g)

$C_f$ = Final aqueous phase concentration (mg/l)

a (l/g), b (l/mg), and $ are the three constants, where $ is less than unity. The above

equation has been used for modeling acetone, p-cresol, p-chlorophenol, 2-propanol, and

propionitrile adsorption data where Calgon's Filtrasorb 300 activated carbon was used as

the adsorbent (Radke and Prausnitz, 1972).

Redlich-Peterson Model : The Redlich-Peterson model is a three-parameter

model given by:

$$\frac{X}{M} = \frac{aC_f}{1 + bC_f{}^{\beta}}$$

(3.6)

where,

X = Moles of adsorbate adsorbed (mol)

M = Mass of adsorbent (kg)

$C_f$ = Final adsorbate concentration (mol/m$^3$)

The three constants are a, b, and $\$$ . The parameter 'a' has the units of m$^3$/kg, b

has the units of (m$^3$/mol)$^{\$}$ , and $\$$ lies between 0 and 1 (Redlich and Peterson, 1959). The

above equation has been used for modeling phenol adsorption from dilute aqueous

solutions onto Amberlite XAD-8 resins (Farrier *et al*., 1979) and  XAD-4 and XAD-7

resins (Itaya *et al*., 1978).


Dubinin-Astakov Model: The Dubinin-Astakov (DA) Model is of the form:

$$\frac{X}{M} = q_m \ \exp\left[-\left(\frac{A}{E}\right)^n\right]$$

(3.7)

where,

X = Mass of solute adsorbed (mg)

M = Mass of adsorbent (g)

$q_m$ = Maximum adsorption capacity (mg/g)

E = Adsorption potential at which the capacity is 36.8% of the maximum

    capacity

n = Heterogeneity of the micropores, represents the curvature of the isotherm

A = Adsorption Potential (kJ), defined by the following equation

$$A = RT \ln (C_s/C) \tag{3.8}$$

where,

R = Ideal gas constant (8.314 J/mol/K)

T = Temperature (K)

$C_s$ = Aqueous solubility (mg/l).

An n value of 1.5 or less represents an adsorbent with heterogeneous pores, while an n value approaching 3.0 represents an adsorbent with homogeneous micropores (Davis and Powers, 2000). The DA equation has been used for the adsorption of phenolic compounds from aqueous solutions onto activated carbon (Stoeckli *et al.*, 2001).

# CHAPTER IV

# CANDIDATE ADSORBENTS

## **Kenaf**

Kenaf (*Hibiscus cannabinus L.*) is an annual, non-wood fiber plant that is in the same family as cotton and okra. The major constituents of kenaf include cellulose, lignin, and hemicellulose (Han, 1999). Under ideal growing conditions, kenaf reaches heights of 12 to 18 feet and yields 6 to 10 tons of dry fiber per acre in a 150-day growing season (Kugler, 1988). The plant stalk is composed of two distinct types of fiber. The outer fiber is called the bast. This fraction comprises roughly 40 % of the stalk's dry weight. The refined bast fiber has an average length of 2.6 mm. The whiter, inner fiber is the core which comprises 60 % of the stalk's dry weight. The core fiber averages 0.6 mm in length. Recent technological development allows for these fibers to be separated (Gowan, 1997). The bast fiber, due to its length and strength has found use in making tea bags, filter paper, high quality writing paper, cordage, and even textiles. The core fiber has potential use as poultry litter and animal bedding. There has also been some efforts to use kenaf as a replacement for styrofoam due to its good insulating properties and biodegradability (Gowan, 1997). Figures 4.1 and 4.2 show the SEM image of kenaf core and kenaf stalk, respectively.

**Peat Moss**

Peat is a yellow to dark brown residue composed of partly carbonized plant material that has accumulated in a water-saturated environment, such as peat bogs (Barnett and Clarke, 1983). Peat is a complex material containing lignin, cellulose, and humic acids as its major constituents. Peat is considered a mineral resource that has been mined and processed for fuel in Ireland and Northern Europe. In the U.S., it is used as a soil conditioner (Cardoso and Clarke, 1985). The peat moss used in this research was a Canadian sphagnum peat. It is an important ingredient that adds vital organic material to all soils. Peat moss naturally retains moisture, giving it a high water holding capacity. It also provides a moderate degree of aeration to soil beds, as long as it is not finely ground (Dueitt, 1994). Also, peat moss has been reported as having a high porosity (Boardsell *et al.*, 1979). The surface functional groups of peat include alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides, which can be involved in the adsorption of pollutants. Figure 4.3 shows the SEM image of peat moss.

**Hay**

The third adsorbent used in the study was hay. Hay is the oldest and most important conserved fodder, which can be processed using simple equipment, manually or with mechanization. Hay contains over 18 % crude fibers and under 20 % crude proteins in dry form. Hay can be made in several forms, depending on the conditions and level of technology applied. The moisture content is reduced from 70-90% to 20-25% or less during

haymaking. Common types of hay include long hay, chopped hay, baled hay, and wafered hay of which, chopped hay is considered to be less bulky and better for mechanical handling (Suttie, 2000). Figure 4.4 shows the SEM image of hay.

### Peanut Hulls

Peanut hulls are the fourth natural adsorbent of interest used in this study. The major constituents of peanut hulls include fiber, cellulose, and lignin (Clark *et al.*, 1999). The porosity of peanut hulls is estimated to be around 62 % and the bulk density to be around 5-7 lbs/ft$^3$ (Brown *et al.*, 2000). Both raw and crushed peanut hulls were tested for their effectiveness as adsorbents. Peanut hulls are an abundant by-product in the southeastern Unites States. Peanut hulls are an inexpensive, renewable resource and are readily available (Brown *et al.*, 2000). Over 4,000,000,000 lbs of peanuts are produced annually in the United States. The vast majority of this crop originates in the south and southeastern states with Georgia being the largest producer followed by Texas and Alabama. Peanut hulls are a waste product of agribusiness and an estimated total of 1,500,000,000 lbs of hulls are produced annually in the United States (National Agricultural Statistics Service, 1997). Figures 4.5 and 4.6 show the SEM images of raw peanut hulls and crushed peanut hulls, respectively.
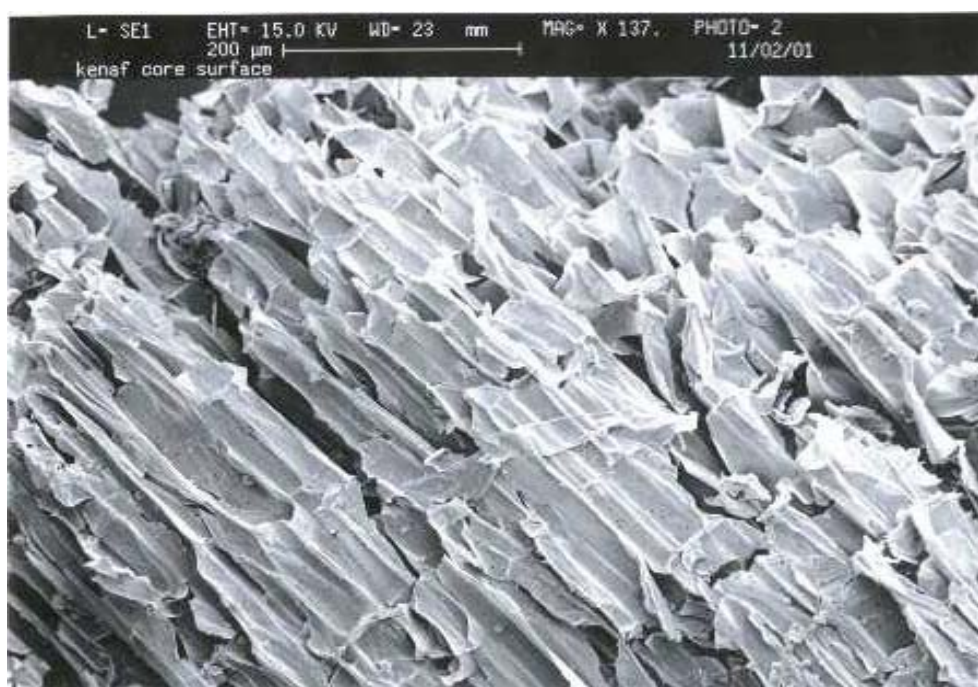
Figure 4.1. SEM image of kenaf core. Magnification : 1 x 137.
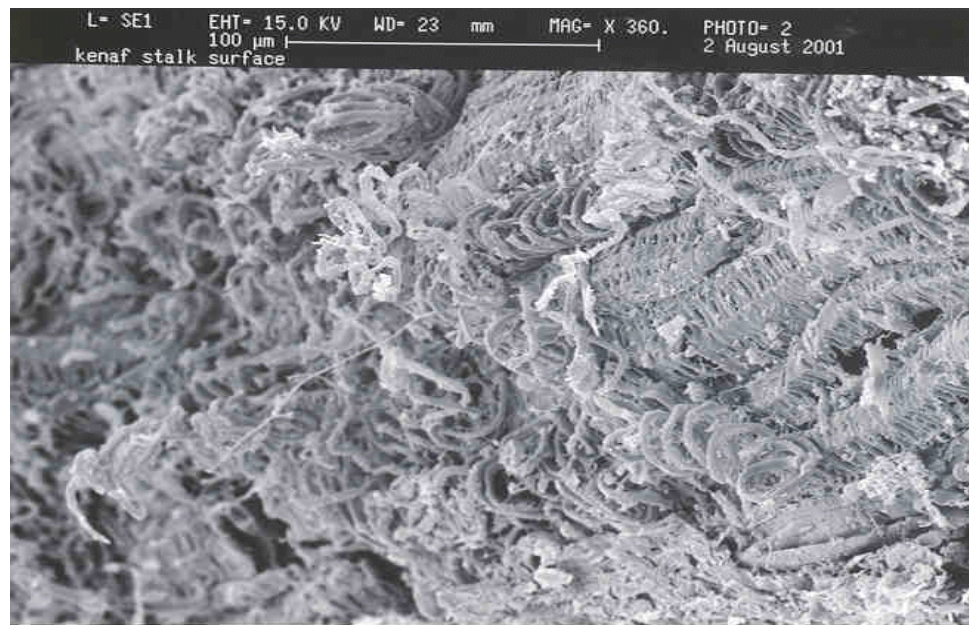
Figure 4.2. SEM image of kenaf stalk. Magnification: 1 x 360.

23
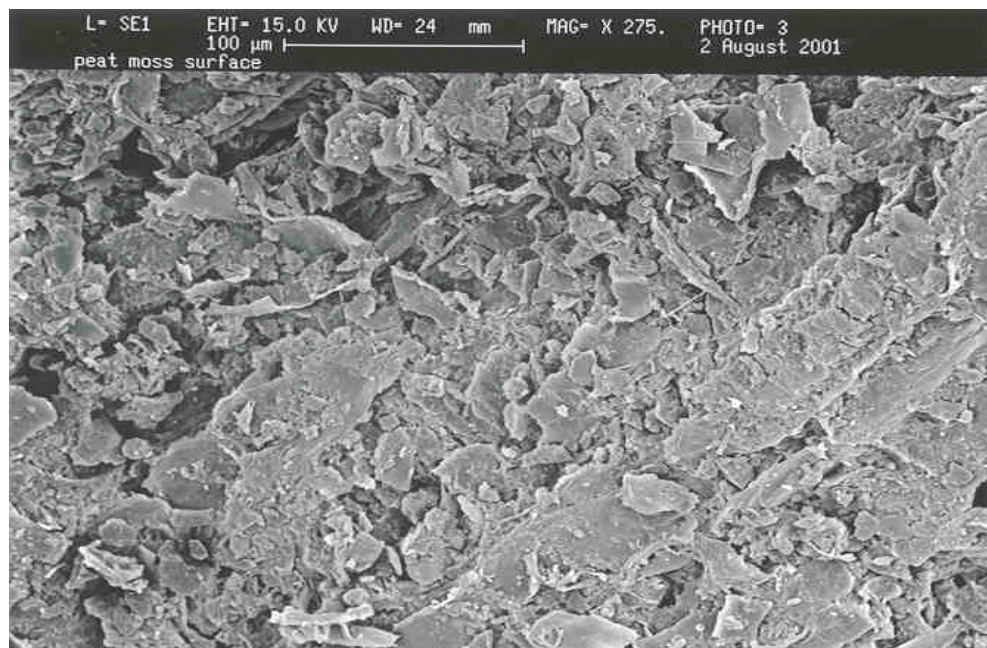


Figure 4.3. SEM image of peat moss. Magnification: 1 x 275
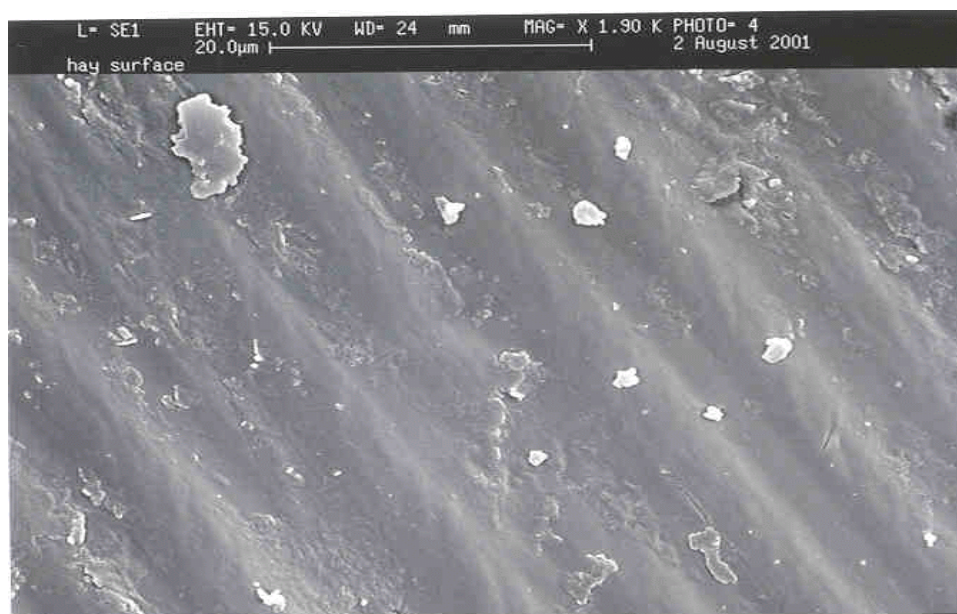


Figure 4.4. SEM image of hay. Magnification: 1 x 1900.
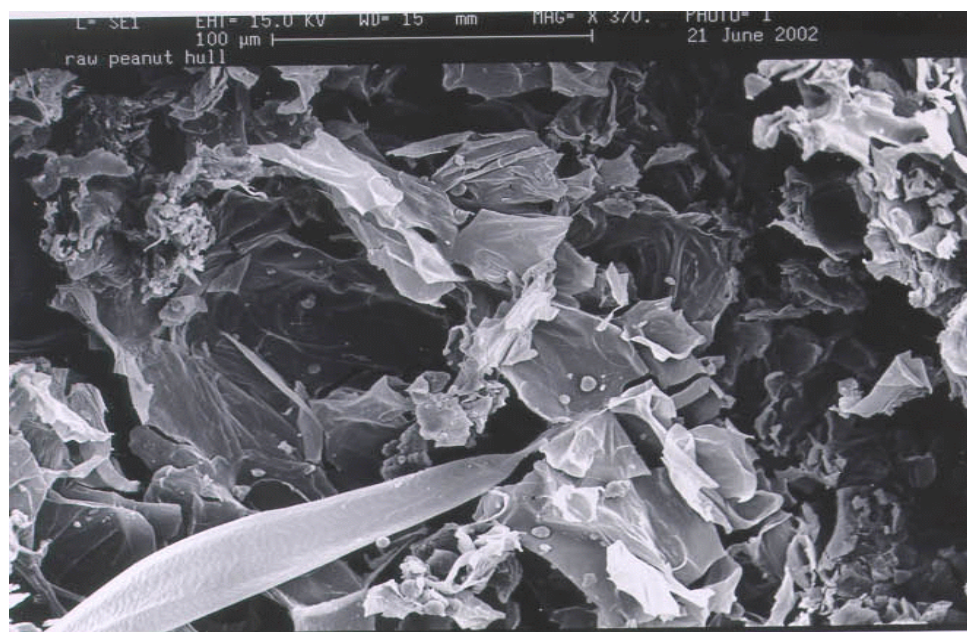
Figure 4.5. SEM image of raw peanut hull. Magnification : 1 x 370.
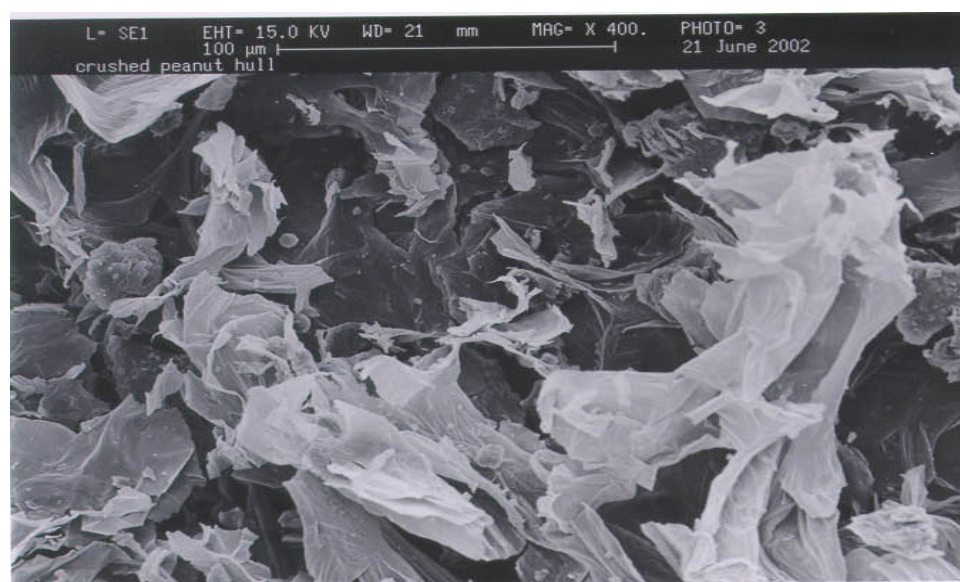


Figure 4.6. SEM image of crushed peanut hulls. Magnification: 1 x 400.

# CHAPTER V

# CANDIDATE ADSORBATES

## 2,4-Dichlorophenol

The primary sources of phenols in natural waters include generation during natural decay processes or releases in the effluents from coking plants, brown coal distillery plants, and the pulp and paper industry (USEPA, 1977). Phenols are used in the synthesis of a number of organic compounds, and this results in their presence in the effluents from many chemical plants. It has been estimated that the concentration of free phenols in unpolluted streams is less than 50 µg/l, while that in rivers receiving industrial and municipal wastewater is frequently greater than 100 µg/l (Zogorski *et al.*, 1976). The desired level for protection of human health based on toxicity data is 3.09 mg/l, while the estimated level for undesirable taste and odor qualities in the ambient water is 0.3 ∶ g/l (USEPA, 1980). Phenols are reported by the USEPA in the 1993 Toxic Release Inventory as one of the top twenty-five chemicals most discharged by US industries (Zappi, 2000). Phenols are listed on many target regulatory lists as a contaminant of primary interest. They have been the subject of many research topics in the past; unfortunately, most of this work was targeted toward high level contaminated waters with little attention focused on low level contamination that now constitutes a large fraction of the phenolic mass released into the environment.

The structure of phenols is similar to a number of pesticides, which resist biodegradation. Roughly twenty five percent of the pesticides on the world market are chemicals, that possess a substituted phenol moiety, which can be cleaved from the molecule through hydrolysis in natural waters (Freistad *et al.*, 1969).

Chlorophenols have found widespread usage in the pulp and paper industry. Due to their toxicity and recalcitrance, they form an important class of environmental pollutants (Colella and Armenante, 1998). Because of their high solubility, they not only contaminate wastewaters and groundwaters but also migrate within different aqueous environments (Smith and Novak, 1987). Chlorophenols also impart an objectionable taste and odor to water (USEPA, 1975).

2,4-Dichlorophenol (2,4-DCP) was chosen to represent chlorophenols. It is a solid at room temperature and is a high production volume feed stock used for the production of herbicides and some other chemicals. Outside of industrial uses, 2,4-DCP is not used, however, small amounts may be present when chlorination converts other phenolic compounds into 2,4-DCP (Agency for Toxic Substances and Disease Registry, 1992). Table 5.1 lists the key physical and chemical properties of 2,4-DCP. Figure 5.1 illustrates the chemical structure of 2,4-DCP.

**2,4,6-Trinitrotoluene**

2,4,6-Trinitrotoluene (TNT) has been the most widely used explosive since the turn of the century. It is a major pollution problem for the Department of Defense (DoD) sites as it has been reported as a contaminant in both groundwater and surface waters. The TNT isomer used in modern explosives technology is 2,4,6-trinitrotoluene. TNT is a yellow odorless solid and does not occur naturally in the environment. It has been used for making explosives due to its advantages, which include low production cost, safe handling, high explosive power, good chemical and thermal stability, and favorable physical characteristics (Zappi, 1995). TNT was first synthesized by Willbrand in 1865 and is considered the major explosive for charges and bombs (Daun *et al.*, 1998). TNT is manufactured by the nitration of toluene through a variety of manufacturing steps. Toluene is nitrated to nitro toluene and then nitrated to dinitrotoluene with subsequent nitration to form TNT, wherein each nitration is carried out in different manufacturing steps. TNT contamination can occur during the purging of solid or molten crude. TNT with 16 percent aqueous sodium sulfite used for removing the secondary isomers of TNT produce a very contaminated wastewater. When the residual TNT particles are rinsed from assembling facilities, wastewater is generated (Zappi, 1995). Germany produced approximately 800,000 tons of TNT during the Second World War (Preuss and Haas, 1988). A half century after this massive production, it still exists in Germany at high concentrations and has migrated into water supplies of the neighboring communities (Haas and Low, 1986). The EPA has determined TNT to be a possible human

carcinogen. Wastewaters from U.S. government arsenals typically contain upto several

hundred ppm's of TNT isomers (Mueller *et al.*, 1993).  The effluent criteria for TNT is

40 : g/l (Wujcik *et al.*, 1992).  The discharge levels set for total nitrobodies in the

effluent is 2 : g/l (CECER, 2002).  Table 5.2 lists the key physical and chemical

properties of TNT and Figure 5.2 illustrates the chemical structure of TNT.

Table 5.1. Physical and Chemical Properties of 2,4-DCP (LaGrega *et al.*, 1994; Dobbs
and Cohen, 1980; Snoeyink *et al.*, 1977)

| | |
|---|---|
| Uses | Feedstock agents for certain herbicides and pharmaceuticals |
| | Moth proofing |
| | Antiseptic |
| | Wood preservative |
| | |
| Properties | Molecular Weight...163 |
| | Melting Point...45 $^0$ C |
| | Boiling Point...210 $^0$ C |
| | Aqueous Solubility...4,500 mg/liter @ 20 $^0$ C |

Table 5.2. Physical and Chemical Properties of TNT (Zappi, 1995)

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Uses                                    Explosives

                                        Textile dyes


Properties                              Molecular Weight...227.13

                                        Melting Point...88.7 $^0$C

                                        Boiling Point...240 $^0$C

                                        Aqueous Solubility...200 mg/liter @ 15 $^0$C

                                        Form at 20 $^0$C...Solid crystal (yellowish)

---
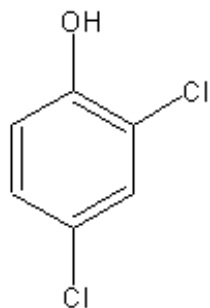
Figure 5.1. Chemical structure of 2,4-Dichlorophenol (2,4-DCP)
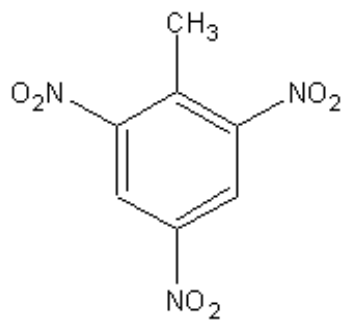


Figure 5.2. Chemical structure of 2,4,6-Trinitrotoluene (TNT)

# CHAPTER VI

# REVIEW OF RELEVANT LITERATURE

## Use of Novel Adsorbents

The use of novel adsorbents is not new.  Activated carbon cost  $2.00/lb.  Due to this economic drawback of activated carbon much work has been done in finding cheaper materials to be used as potential substitutes.  Cheap materials such as peat (Chaney *et al.*, 1979), fly ash and coal (Gupta *et al.*, 1990), olive wood (Gonzalez *et al.*, 1998), peanut hulls (Brown *et al.*, 2000 ; Periyasamy and Namasivayam, 1994), lignin (Srivastava *et al.*, 1994),  minerals (Handerlein and Schwarzenbach, 1993), bleaching earths (Pollard *et al.*, 1992), clays and fertilizer waste (Srivastava *et al.*, 1989) have been tested for use as adsorbents.

Kenaf : Kenaf has been used for adsorbing toxic heavy metals (nickel, copper, zinc, and cadmium) from storm water (Han, 1999).  The adsorption potential of lignocellulosic fibers such as kenaf was found to be related to their sugar content, extractives composition, lignin content, and physical property.  It was found that a decrease in the lignin and cellulose content contributed to a lower density and easy accessibility of ions to the reactive sites on kenaf's surface, thus increasing the adsorptive capacity (Han, 1999).

Peat moss : Peat has been largely used for the adsorption of heavy metals from wastewaters due to its excellent ion exchange properties ( Belkevich *et al.*, 1976).  This has led to the examination of the potential for peat to act as an adsorbent for the purification of contaminated wastewaters (McKay, 1996).  The effectiveness of two peat samples for adsorbing selected heavy metals from aqueous solutions were tested.  It was found that peat had a good adsorbing capacity for heavy metals (Cardoso *et al.*, 1985). Sphagnum peat was used to adsorb copper, cadmium, and zinc from aqueous solution (Allen *et al.*, 1992).  Peat was also found to have the ability to treat colored effluents with a good adsorption capability (Allen *et al.,* 1988 ; Allen and McKay, 1987).  Peat has been used for the adsorption of dye house effluent (Leslie, 1974).  The adsorptive capacities of peat moss for two industrial textile dyes were studied and the Freundlich Model was applied successfully.  It was found that peat moss provided  effective removal of the dyes. (Nawar and Doma, 1989).

Hay : There has been some effort in using a tropical grass as a feedstock for making adsorbents (Chughtai *et al.*, 1987).  After impregnation with either commercial grade $H_2SO_4$ or $ZnCl_2$, the material was pyrolised at 400-750 $^{\circ}$C in the absence of air and the products were screened for methylene blue adsorption.  The adsorbent exhibited a dye adsorption capacity of 223 mg/g.

Peanut hulls : Peanut hulls have been studied for their effectiveness as adsorption media for removing heavy metal ions from wastewater streams (Waiss *et al.*, 1973 ; Henderson *et al.*, 1977 ; Okieimen *et al.*, 1991). More recently, the potential of peanut hull pellets to adsorb metal ions from wastewater were tested and the performance of raw peanut hulls was compared to a commercial grade ion-exchange resin (Brown *et al.*, 2000). The capacity of raw peanut hulls and peanut hull pellets was found to be lower than the ion-exchange resin; however, it was concluded that the low cost of the raw peanut hulls and peanut hull pellets could make them an attractive option for the treatment of low-strength metals contaminated waste streams. No attempts were made to improve the capacity of the adsorbents nor was the effect of pH and temperature evaluated during this study.

Tire rubber : The adsorptive capacity of raw tire rubber has been evaluated by Kim *et al.,* (1997). The sorption capacity of ground tires were found to be 1.1 to 4.4 % of the capacity reported for GAC. Chloroform, ethylbenzene, methylene chloride, toluene, 1,1,1-trichloroethane, trichloroethylene, and m-xylene were used as the adsorbates within a water matrix. The low adsorptive capacity of tire rubber when compared to GAC was attributed to the low surface area of ground tire granules (which ranged from 0.16 to 0.56 $m^2$/g). Both the Freundlich and the Linear Model ($X/M = kC_f$) were evaluated for fitting the experimental data. Neither of the two models indicated any appreciable difference

with their respective correlations for the range of concentrations used in the tests (20 mg/l to 50 mg/l).

Rubber from stripped tires has reportedly been used as an adsorbent (Luchesi and Maschio, 1983). Waste car tyres were used for their high carbon content. A variety of atmospheres were used to produce carbon from the rubber obtained from stripped tyres. The surface area of the resulting adsorbent was found to be 320 $m^2$/g. The adsorbent demonstrated Freundlich-like behavior for the removal of Orange II and Acid Black 24 dyes from the aqueous phase. A commercial powdered activated carbon prepared from the waste tire rubber exhibited a high affinity for aqueous phase phenol; although, the surface area was only 193 $m^2$/g (Paprowicz, 1990).

Polymers: The adsorption of acenaphthene from aqueous solutions using two commercial polymers were studied by Eichenmuller *et al.,* (1997). The Freundlich Model had a smaller standard deviation than the Langmuir Model for fitting the data. The adsorptive capacity of the organic polymers was found to be comparable to that of an activated carbon. The adsorption capacities of different polymers were studied by Wightman *et al.,* (1971). The adsorption process was considered to be taking place between three components- adsorbent, adsorbate, and solvent. The adsorbent surfaces were found to vary with respect to surface and surface energy as gauged by hydrophilicity. It was found that the amount of phenols adsorbed per unit area by the

solid increased as the surface energy of the solid decreased (i.e. as the hydrophilicity of the adsorbent surface decreased).

Rice Hulls : Chemical ($ZnCl_2$ and $H_3PO_4$) and physical ($CO_2$) activation procedures have been used to prepare rice hull - based adsorbents (Tanin and Gurgey , 1988).  The surface area was found to be 482-788 $m^2$/g.  Methylene blue adsorption was found to be well modeled using the Freundlich Model.  The adsorptive capacities of rice hulls for two industrial textile dyes were determined by Nawar and Doma (1989).  The Freundlich Model was successfully applied.  It was found that the rice hulls displayed effective removal of the dyes.

Waste By-Products : Studies have been performed on the removal of substituted phenols by carbonaceous adsorbents obtained from fertilizer waste (Srivastava *et al.*, 1997).  Using 2,4-dinitrophenol (DNP) as the adsorbate, it was found that adsorption was constant from pH 2.0 to pH 4.0, with a decrease in adsorption noted beyond a pH of 4.0. This observation was attributed to the pKa value of the adsorbate (3.96), since the non-dissociated species of the adsorbate was likely preferred by the negatively charged surface of the carbonaceous adsorbent.  The correlation coefficient for the DNP  data was found to be more than 0.95 for both the Langmuir and the Freundlich Models, indicating that the data could be equally well represented by either model.

Activated slag from blast furnace waste material has been used for the removal of copper and nickel (Gupta, 1998). The correlation of experimental data was found to be quite good using both the Freundlich and Langmuir Models.

The effectiveness of solid residues from both an olive-mill waste and of pyrolized oil shale was evaluated for removing methylene blue (a cationic dye) and methyl orange (an anionic dye) from aqueous solutions (Abu-El-Sha'r *et al.,*1999). The respective performance of each were compared to that of a coconut shell-based activated carbon. The oil shale sorbent was found to have the highest adsorption capacity for methylene blue, since methylene blue dissociated into its ionic form. As an ionic form, the dye's positive ions interact with the intra-surfaces of the anionic sorbent. Since methyl orange dye dissociates within aqueous solutions into negatively charged ions, the ions were repelled by the like charged sorbents since adsorption is the result of Van der waals forces.

The adsorptive capacity of fly ash for phenol, cresol, and a combination of phenol and cresol was studied by Kumar *et al.,* (1987). They found that fly ash had removal efficiencies of 40, 45, and 45% w/w for 50 ppm aqueous solutions of the adsorbates, respectively. At low phenol concentrations, adsorption onto fly ash was considered satisfactory, but kinetic studies indicated that longer equilibrium contact times were required when compared to activated carbon.

**Adsorption of Phenols**

A great deal of research has been performed on the adsorption of phenols and chlorophenols onto activated carbon. Adsorption isotherms for twelve mono-,di-, and tri-chlorophenols from aqueous solutions on wood-based and lignite-based carbons have been studied (Colella and Armenante, 1998). The Freundlich Model was successfully used to model these data. The Langmuir Model was found to have a very poor fit. A wide range of initial concentrations were tried ranging from 100 to 4,000 mg/l. The adsorptive capacity for activated carbon in adsorbing 2,4-DCP was found to be 502 mg/g. Particle size did not appear to play a significant role on chlorophenol adsorption; although, larger particles were associated with a slightly diminished adsorption capacity.

Isotherms for 2,4-DCP adsorption onto activated carbon were generated and the Freundlich Model was used to fit the experimental data (Dobbs and Cohen, 1980). The adsorptive capacity was found to be 157 mg/g ( $C_f$ = 1 mg/l) and 1/n to be 0.15 at a pH of 5.3.

Adsorption data for chlorophenols onto activated carbon were generated by Snoeyink *et al.,* (1977). The Langmuir Model was found to be inadequate for fitting single solute adsorption data over a broad concentration range. It was also found that there was a significant reduction in the adsorptive capacity (50 percent) of one chlorophenol in the presence of another chlorophenol.

Adsorption equilibria of eight phenolic compounds over a wide range of concentrations ranging from 40 mg/l to 500 mg/l onto activated carbon at 303 K were

generated by Juang *et al.,* (1996). Higher adsorption capacities were found for the chlorinated phenols when compared to the methyl-substituted phenols. The Langmuir Model was valid only at higher concentrations. The Freundlich Model was found to provide a better fit than the Langmuir Model.

The kinetics of adsorption of phenols by granular activated carbon were studied by Zogorski *et al.,* (1976). It was observed that 60% to 80% of the ultimate adsorption occurs within the first hour of contact followed by a very slow approach to the final maximum equilibrium concentration. They found that at an initial concentration of 330 : mole/l of 2,4-dichlorophenol the rate of adsorption was limited by external transport of the adsorbate molecules onto the carbon surface, but at a higher concentration of 1900 : mole/l the rate-limiting step was found to be due to intra- particle diffusion.

The solution pH plays a significant role in the adsorption of chlorophenols. It was found that chlorophenols were adsorbed very strongly by activated carbon at the μg/l level, which is near the threshold odor limit (2 μg/l) for these compounds. The extent of adsorption of 2,4-DCP was found to be a function of pH (Snoeyink *et al.*, 1977). The neutral species of 2,4-DCP predominate at pH below its pKa value (7.85) and adsorbed more strongly than the anionic species. It was found that the dissociated molecules for aromatic compounds at pH values above the pKa value are less strongly adsorbed than the undissociated form and that the maximum adsorption occurs at a point where pH = pKa for each compound (Ward and Getzen, 1970). The kinetics of adsorption of phenols by granular activated carbon were studied and it was found that the rate of adsorption

was decreased at pH levels greater than the pKa of the adsorbates (Zogorski *et al.*, 1976).

The porosity of the adsorbent material also plays a significant role in the adsorption of aromatic organics. There have been discrepancies in the adsorptive capacity ordering of phenols and chlorophenols, which is attributed to be differences in the pore structure between the activated carbons and other adsorbents used. The ordering was found to be phenol > 4-cholorophenol > 2,4 dichlorophenol by Caturla *et al.,* (1988); whereas, the ordering was found to be 2,4-dicholorophenol > phenol > 4-chlorophenol for the adsorption data determined by Jossens *et al.*, (1978). In another study, it was observed that the ordering was 4-chlorophenol > phenol > p-cresol on a commercial resin. (Itaya *et al.*, 1978). It was concluded that the micropore size and pore distribution play an important role in the adsorption of phenols onto adsorbents.

The adsorption of substituted phenols onto activated carbon produced from olive stones has been studied by Caturla *et al.,* (1988). The adsorption process was found to be predominantly controlled by the porosity of the carbon when the degree of activation is low and when the carbon has a wide micro porosity. The adsorption of phenols were affected by the chemical nature of the carbon as surface pH increased with the extent of activation. Adsorption was also found to be affected by the constituents of the aromatic ring, which modify the electron density of the aromatic ring.

The adsorption equilibria of aqueous phenol onto activated carbons were studied by Seidel *et al.,* (1985). At higher temperatures more phenol is adsorbed than at lower temperatures. This was attributed to a higher packing density of phenol within the pores

at the higher temperature. An interesting conclusion was made that the adsorption of

phenolic compounds was an endothermic process. As the rate of removal of the

adsorbate increased, the temperature of the system was increased. The activation energy

of phenol and 2,4-dichlorophenol was reported to be 1.6 kcal/mol and 2.2 kcal/mole

(Zogorski *et al.*, 1976).

The presence of surface functional groups is also an important factor to be

considered in the adsorption of phenols onto adsorbents. The presence of dissolved

oxygen increased the adsorptive capacity of activated carbons for phenolic compounds

(Tessmer *et al.*, 1997). This increase in adsorptive capacity was attributed to the

oligomerization of the compounds through oxidative coupling reactions. The presence of

acidic functional groups on the surface of the carbons impacted the ability of activated

carbon to adsorb phenolic compounds under oxic conditions and the presence of oxygen-

containing basic groups such as chromene-type and pyrone-type was a key factor in

promoting irreversible adsorption. The presence of molecular oxygen reportedly

increased the adsorptive capacity of GAC for phenolic compounds by three fold (Vidic *et

al.*, 1993). They also found that an appreciable amount of oxygen is consumed during the

adsorption of phenolics. The acidic oxygen surface complexes decreased the

chemisorption of phenols (Magne *et al.*, 1986). The adsorption of phenols was found to

greatly decrease due to the hydration of the surface functional groups, resulting in water

complexes blocking the pore entrances thus reducing the surface area available for

adsorption. At high adsorbate concentrations, it was found that the interactions between

the adsorbate molecules affected the adsorption process more than the adsorbent-

adsorbate forces (Couglin *et al.*, 1968) .


### **Adsorption of TNT**

Previous studies in the adsorption of TNT have primarily used activated carbon as

the adsorbent. Studies have been focused on determining the adsorptive capacity rather

than studying the adsorption equilibria. US rmy Corps of Engineers (US Army Corps of

Engineers, 2000) have shown explosives removal by GAC to be more than 90%.

Wujcik *et al.*, (1992) have studied granular activated carbon pilot treatment for

treating groundwater contaminated with explosives.  It was found that the removal of

explosives from groundwater using GAC was feasible.  Freundlich constants for two

types of activated carbon (Norit Hydrodarco 4000 and Atochem, Inc. GAC 830) were

determined for TNT adsorption.  The Freundlich constants for Hydrodarco 4000 was

reported as 128 mg/g (k) and 0.828 (1/n).  The Freundlich constants for Atochem, Inc.,

GAC 830 was reported as 136 mg/g (k) and 0.642 (1/n).

The adsorption of explosives was found to be higher at neutral pH (7.0) than at

acidic pH (4.0) (Wujcik *et al.*, 1992).  Also, a contrasting result was reported  that the

adsorption of explosives on granular activated carbon was higher at lower pH

(USATHAMA, 1987).

Activated carbon used for adsorbing TNT was reported to have a 1/n value of

0.14 (Schulte *et al.*,1973).  The study found that an initial concentration of 83,000 : g/l

was reduced to 1,000 : g/l after adsorption. In another study, a loading capacity of 6 – 10

mg of TNT/g of carbon for carbon adsorption was used to reduce an initial concentration

of 246 : g/l to 2 : g/l (Fleming *et al.*,1995) .

GAC has been found to have a loading capacity of 108 mg/g for RDX as the

primary contaminant in water. An increase in the concentration of explosives in the

influent significantly decreased the service life of the GAC. The adsorption of explosives

onto GAC was found to be significantly hindered by fouling due to the presence of

natural organic matter(NOM) in the influent stream (Lee *et al.*, 1998).

Since there is a potential  risk of explosion associated with the regeneration of

activated carbon after treatment with explosives, the use of biodegradation to decrease

the frequency of GAC replacement was proposed by Speitel (1999). It was suggested

that biodegradation of high explosives in the GAC may convert the material from a

hazardous waste to a non-hazardous waste.

The U.S. Army Environmental Center (USAEC), the Industrial Ecology Center

(IEC) of the U.S.Armament Research, Development , and Engineering Center (ARDEC),

and Concurrent Technologies Corporation (CTC) have conducted research on pink water

treatment. Pink water contains TNT in its commonly used isomeric form, 2,4,6-TNT

(Zappi, 1998). The CTC screened 34 potential technologies for treating pink waters and

selected the GAC Thermophilic Biological Process for use in the regeneration of spent

GAC within columns using an in-situ approach thus avoiding the risks associated with

the handling and incineration of the spent carbon. The GAC column was heated to 55 $^{0}$ C

and the biodegradation of the adsorbed pollutants was initiated by circulating explosives-degrading organisms through the column.  The bioreactor fluid mainly contained natural organisms and associated enzymes.  The life of the GAC  was extended by at least five regenerations (US Army Environmental Center, 2000).

There have also been studies where plants have been used to adsorb TNT. Preliminary studies have shown that plant cells can remove TNT from solution (Mueller *et al.*, 1993).  The use of aquatic plants to transform TNT have been tested by Hughes *et al.*, (1997).  Although mineralization was not observed, the plant material  transformed a large percentage of the TNT.

## Surface Activation to Enhance Adsorption

Surface activation techniques enhance the surface characteristics, such as surface area, porosity, and the number of surface functional groups (carbon/oxygen), which are known to enhance adsorption (Puri, 1983; Cooney, 1999).  Previous studies have focused on the use of ozone, hydrogen peroxide, deashing, and chemical activation  to increase the surface area of the adsorbent and to increase the number of surface functional groups (Puri, 1983; Puri, 1966; Puri, 1972; Gomez, 1996; Vazquez,1994).

Treatments; such as, deashing with a hot HF-HCl mixture, burn-off using oxygen under low pressures of 10-20 torr at 600 ºC, and exposure to ozonized oxygen at ambient temperature were studied by Puri (1983).  These treatments increased the surface area of activated carbons as well as sugar and coconut shell charcoals and subsequently

enhanced the adsorption capacity toward phenols within the aqueous phase.

When activated carbons were oxidized in concentrated nitric acid, acidified potassium persulfate, aqueous hydrogen peroxide, or moist air at 285 $^0$C, it was found that acidic surface oxides were formed which increased the effectiveness of the carbon for alkaline pollutants within wastewaters (Puri, 1983). Studies have shown that the number of adsorption sites can be enhanced by surface oxidation followed by evacuation treatment of the adsorbent at 700 $^0$C (Puri *et al.*, 1972).

Deashing lead to an appreciable increase in the surface area of the activated carbon and treatment with the hot HF-HCl mixture was found to cause adequate cleansing of the micropores making additional surface area available for adsorption (Puri, 1983). When the activated carbon was ozonated, small losses of carbon were observed, but there was an appreciable increase in the surface area (Puri, 1983). The surface area value for activated carbon was found to increase with increasing ozonation time but progressively was reduced when the treatment was continued beyond 4 to 6 hours. The loss in surface area after increased ozonation time was attributed to the loss of extremely fine particles that are primarily responsible for the surface area, to get gasified and lost from the surface during the ozonation process of the adsorbent (Puri, 1983).

Activated carbons from Spanish coals have been prepared by chemical activation with alkali and alkaline-earth hydroxides (Gomaz *et al.*, 1996). KOH and NaOH activation procedures resulted in $N_2$ apparent surface areas as high as 2500 m$^2$/g. Also, a pyrolysis temperature of 700 $^o$C resulted in the production of activated carbons with a

wider pore distribution as compared to the carbons pyrolized at 500 ºC. The main

advantage with chemical activation compared to physical activation was due to the fact

that chemical activation can be done at a lower temperature range (400-700 ºC) and

requires a shorter time. The drying process of the carbons was found to greatly favor the

activation process due to porosity development.

*Pinus pinaster* bark has been pretreated with acidified fomaldehyde solution prior

to adsorption. When used an adsorbent it was found that the equilibrium data was

successfully correlated by the Freundlich Model. The adsorptive capacity of the bark in

adsorbing toxic metal ions from wastewater was also found to be comparable to

commercially available adsorbents (Vazquez *et al.*, 1994).

# CHAPTER VII

# MATERIALS AND METHODS

## **Materials**

The test adsorbates used in this study were 2,4-DCP and TNT. 2,4-DCP was obtained from Aldrich Chemical Company (Milwaukee) in solid form ( 99% purity). TNT was obtained from Chem Service (Pennsylvania) in solid form ( 99% purity). Test solutions were made by accurately weighing 2,4-DCP and TNT and dissolving into distilled water. The solution was mixed using a magnetic stirrer for a week to allow complete dissolution of the compounds. Stock solutions were left for mixing in Erlenmeyer flasks until isotherm experiments or column studies were performed.

The natural adsorbents used in the study were kenaf, peat moss, hay, and peanut hulls. Kenaf was obtained in two forms, the core and stalk from the Mississippi Agricultural and Forestry Experiment Station (MAFES) at Mississippi State University. Kenaf stalk material was in fibrous form and used as such. Peat moss was a Canadian sphagnum peat obtained from Walmart. Hay was obtained from a farm in Starkville, Mississippi. Hay was chopped manually (approximately 10 mm in length) before being used for the experiments. Peanut hulls were obtained from the University of Alabama at Tuscaloosa. Both raw (whole peanut hull) and crushed peanut hulls were used for the study.

All the adsorbents were dried at 100 $^0$ C for 24 hours in a Fisher Scientific

isotemp oven.  The adsorbents were then stored in Ziploc bags and placed in a Sanplatec

dessicator until experiments were performed.  The adsorbents except hay were used as

such and no sizing was performed.  The bulk densities of the candidate adsorbents were

determined by filling a 100 ml graduated cylinder with the candidate adsorbents and

weighing the known volume.  The bulk densities of the candidate adsorbents were

reported as lb/ft$^3$.  The surface area of kenaf core was determined by BET analysis using

nitrogen in  an Autosorb 1 from Quantachrome Corporation.  The surface area analysis

was performed by Dr. Hossein Toghiani and Venkata Ramesh Chilukuri (Mississippi

State University).


**Methods**

Equilibrium Experiments: Kinetic experiments were performed to determine the

equilibrium time required for the adsorbents to reach adsorption equilibrium.  Kinetic

runs using 2,4-DCP and TNT were performed for all the adsorbents.  Kinetic experiments

consisted of placing about 0.40 grams of each adsorbent in 60 ml I-CHEM glass vials.

All experiments were run in duplicate.  The experiments were performed at room

temperature (25 $^0$C) and at a pH of about 5.0 (distilled water).  A 40 ml aliquot of the

adsorbate solution was added to each vial and the vials were placed on a Burell wrist

action shaker.  Glass beads were added to each vial to enhance mixing.  Aqueous samples

were collected at different time intervals and analyzed for each adsorbate.  TNT and 2,4-

DCP samples were vacuum filtered using a Gast vacuum pump and filtration equipment. A 0.1 micron Pall glass fiber filter was used for filtration of the samples prior to analysis. A blank solution, serving as an experimental control, contained only the adsorbate solution which was carried throughout the entire process. No significant reduction in the adsorbate concentration was observed during the experimental run for the control.

Adsorption Isotherms: Adsorption isotherms were generated as a means of assessing the adsorptive capacity of the adsorbents. Adsorption isotherm data were generated for 2,4-DCP and TNT using standard 60 ml I-CHEM glass vials. Adsorbents were weighed and placed in the separate glass vials with different doses of adsorbents placed in each vial. All the samples were duplicated. The experiments were performed at room temperature (25 $^0$C) and at a pH of about 5.0 (distilled water). About 40 ml of the adsorbate solution was added to each of the glass vials. Glass beads were added to each vial to enhance mixing. The vials were placed on a Burell wrist action shaker and the samples were shaken until the equilibrium time determined during kinetic runs was reached. For the majority of the experimental runs the concentration of 2,4-DCP and TNT used for were in the range 10 mg/l - 40 mg/l, but isotherms were also conducted with concentrations as low as 2 mg/l and as high as 70 mg/l. The purpose of using such a wide range in concentration was to check the effectiveness of the adsorbents within a wide range of concentrations. After the equilibrium time was reached, the samples were vacuum filtered using a 0.1 micron glass fiber filter prior to high performance liquid

chromatography (HPLC) analysis.

Blank samples containing only the adsorbate solution were used to determine if the experimental process considerably reduces the concentration of the pollutant. It was found that significant amounts of the adsorbate was not lost in the procedure. Experiments with blank solutions containing a constant amount of adsorbent and distilled water were performed to determine if the experimental procedure induces a significant peak to hinder with the retention time during sample analysis with the HPLC. It was found that no peaks were found at the retention time of the adsorbates used for the study. Filter paper control experiments were performed to determine if the filter paper used for filtering the solution before instrumental analysis had a significant effect in retaining the adsorbate. It was found that no adsorbate concentration was retained by the filter papers used.

To ensure clean laboratory usage of glass ware, cotton plugged disposable pipettes were used for all the sampling procedures. All the glass wear used for the experiments were cleaned with tap water and rinsed with distilled water and dried before being used for experiments.


Dynamic Column Experiments: In this part of the study, kenaf core, kenaf stalk, and raw peanut hulls were used as adsorbents. These adsorbents were readily available and facilitated good flow of the influent through the column. The apparatus used for the study was a 50 mm glass column with minimum effective length of 600 mm and

approximate capacity of 1.16 liters each.  The column was operated under upward flow conditions.  The setup used for the continuous flow studies is shown in Figure 7.1. The columns were purchased from Ace Glass Inc.  Easy- Load II peristaltic pump with an adjustable occlusion for the pump head coupled with a variable speed modular drive were used for the study to accurately maintain the flow rate.  Tygon extended life silicone tubing was used.  The pumps and tubing were purchased from Cole Parmer Instrument Co., Illinois.  The flowrate at the outlet of the columns were checked with a graduated cylinder and timer.  The inlet solution containing the pollutant was pumped from a 20 liter glass container used as an influent reservoir.

Each end of the column was packed with 5mm borosilicate glass beads to prevent movement of the adsorbent within the column.  Polyethylene filter discs were used to keep the glass beads in position.  The adsorbent material was allowed to settle under their own weight and gentle manual tapping during packing ensured uniform distribution of the material in the column.  Before startup, the column was operated for 2 hours by passing distilled water through the adsorbent since agricultural materials are hydrophobic.  This allowed the adsorbent particles to become wet prior to receiving the organic influent and removal of the bulk of the fines (Larry, 1983).  The experiments were initiated when the adsorbate solution was placed in the feed bottle.  Sampling from the outlet of each column was performed at various time increments.  Two samples were drawn at each designated and the samples were averaged to obtain the outlet concentration of the effluent from the columns for that sample time.  The samples were

filtered prior to HPLC analysis.  Since the flow rate could have an effect on the

continuous column operation, different flow rates were used with bed depth remaining

the same.

Control experiments for continuous flow studies were performed by flowing only

distilled water through the columns at the highest flow rate used during the experimental

run to determine if the adsorbent leaches any material which could hinder chemical

analysis.  During HPLC analysis no peaks were found at the retention time of the

adsorbates used for the study.

Ozone Treatment: Ozonation of the adsorbents were conducted as an effort to

create surface functional groups (carbon/oxygen groups) by oxidation and possibly

increase the surface area of the adsorbent; thus, enhancing the adsorption characteristics

of the adsorbent (Puri, 1983; Cooney, 1999).  Ozonation of the adsorbents was conducted

in 2 liter Erlenmeyer flasks in the form of a batch reactor with the adsorbent material

being mixed with distilled water. Effective mixing was achieved using a Fisher Scientific

Thermix Model 120 S stirrer.  Figure 7.2 shows the ozonation setup used for the

experiment.  Ozone was generated by a laboratory ozone generator Model  LC-1234

(Ozonology Inc., Evanston, Illinois).  This ozone generator is a corona discharge unit that

utilizes four stainless steel electrodes inside borosilicate glass dielectrics with copper

jacketing.  Within the four cells ozone is generated and is regulated by a single primary

voltage autotransformer.  Gas flow is controlled by a rotometer within a range of 1-6

scfh. The off gas outlet from the batch ozonation reactor was connected to a bottle containing ozone destructing carrulite catalyst pellets. Ozone pretreatment of the candidate adsorbents was conducted at contact times of 1, 2, and 4 hours to determine the effect of ozonation exposure on adsorption. After pretreatment, the adsorbents were filtered and dried for 24 hours at $100\,^{0}C$ and then stored in ziploc bags and placed in a desiccator until further isotherm experiments were conducted.

Peroxone Treatment: Combination of ozone and hydrogen peroxide were tested to study the possibilty of peroxone treatment as a surface activation technique to enhance adsorption. Peroxone is described elsewhere (Zappi, 1995). Peroxone treatment of the adsorbents was conducted using the same procedure as ozonation except that 500 ppm hydrogen peroxide was added to the batch reactor containing the adsorbent before sparging ozone. The hydrogen peroxide was purchased from Aldrich Chemicals (30 % weight, density 1.11). Peroxone treatment of the adsorbents was conducted for 2 hours. After pretreatment the adsorbents were filtered and dried for 24 hours at $100\,^{0}C$ in a oven and stored in ziploc bags and placed in a desiccator until further isotherm experiments were conducted.

Ultrasound Treatment: A combination of ultrasound and ozone treatment was conducted to study the feasibility of ultrasound and ozone as a surface activation technique to enhance adsorption. Figure 7.3 shows the setup used for this purpose.

Ozone was sparged through the reactor continuously along with ultrasound.  An

ultrasonic horn capable of resonating at 20 kHz was used to generate ultrasonic waves at

40 amplitude cycles.  The combination of ultrasound and ozone was performed at contact

times of  2  and 4 hours.  After pretreatment, the adsorbent was filtered and dried for 24

hours at 100 $^0$ C and stored in ziploc bags and placed in a desiccator until further

isotherm experiments were conducted.

### Analytical Methods

2,4-Dichlorophenol: 2,4-Dichlorophenol was analyzed following EPA Method

604 using a Waters model HPLC.  A 515 model pump and pump control module was

used.  A Symmetry model column 3.9 mm x 150 mm, $C_8$ 5 :  m column was used along

with a Waters 2487 dual wavelength absorbance detector.  2,4-DCP was detected using

UV at 280 nm.  A mobile phase of 1% acetic acid in water and 1% acetic acid in

acetonitrile was used with gradient flow.  A ten point calibration curve was used for

sample quantification.  The standards were diluted from a  500 :  g/ml in methanol

standard to obtain a series of standards of varying concentrations.  The calibration curve

thus created had a correlation coefficient of  more than 0.99. The processing method was

checked periodically by injecting known standards (Catalog Number: 48690-U) obtained

from Supelco Inc. (Pennsylvania).

2,4,6-Trinitrotoluene: TNT was analyzed using a Hewlett Packard Model 1100

HPLC.  A  15 cm x 4.6 mm, 5 :  m Supelcosil LC-8 column was used along with a Diode

Array Detector. 2,4,6-Trinitrotoluene was  detected at 254 nm.  A mobile phase of  82% water and 18% isopropanol was used.  A ten point calibration curve was used for quantifying TNT samples.  The standards were prepared from an EPA 8330 mix A 100 : g/ml in acetonitrile standard and diluted to obtain a series of standards with varying concentrations.  The calibration curve thus created had a correlation coefficient of more than 0.99.  The processing method was checked periodically by injecting a known standard (Catalog Number: 4-7283) obtained from Supelco Inc. (Pennsylvania).
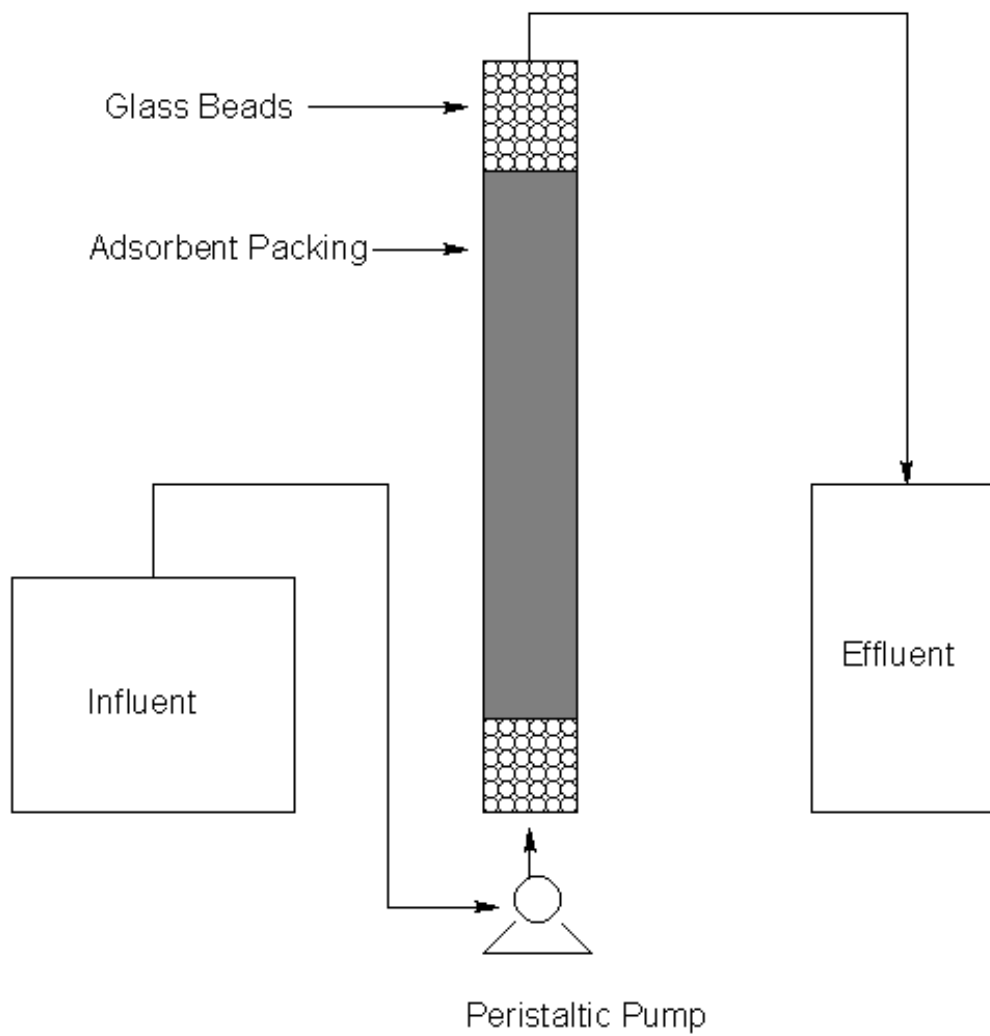
Figure 7.1. Continuous column studies setup.
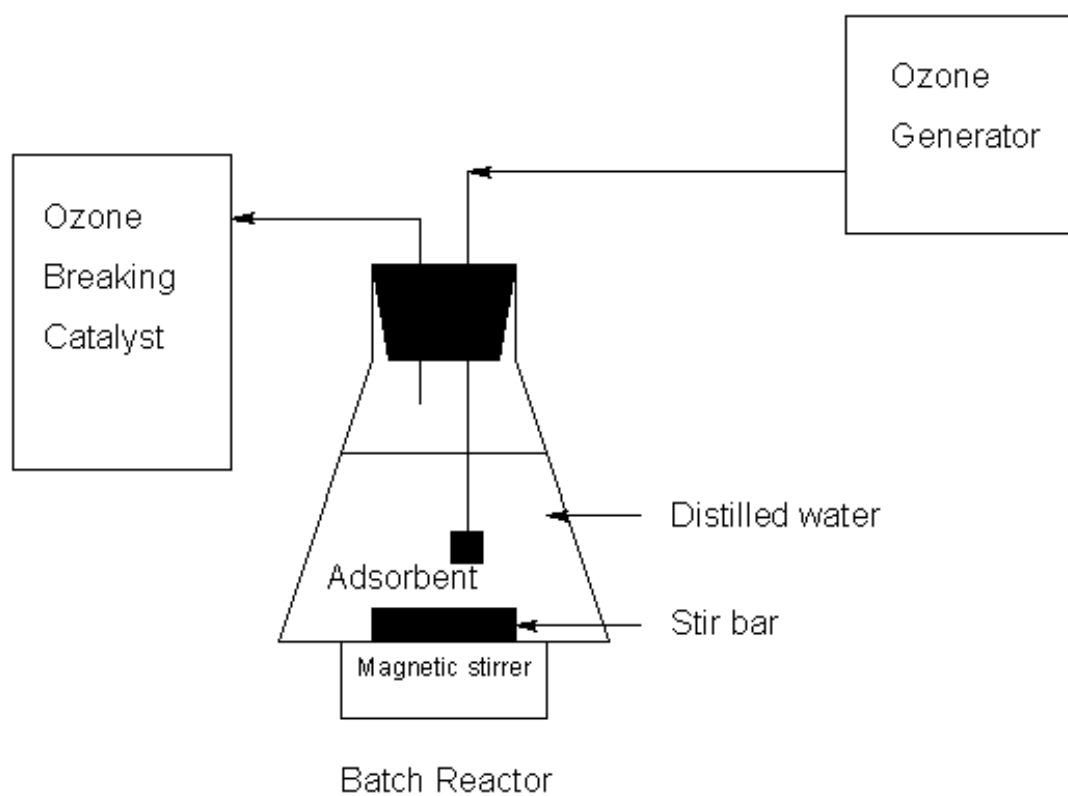
Figure 7.2. Setup for ozonation and peroxone treatment of the adsorbents.
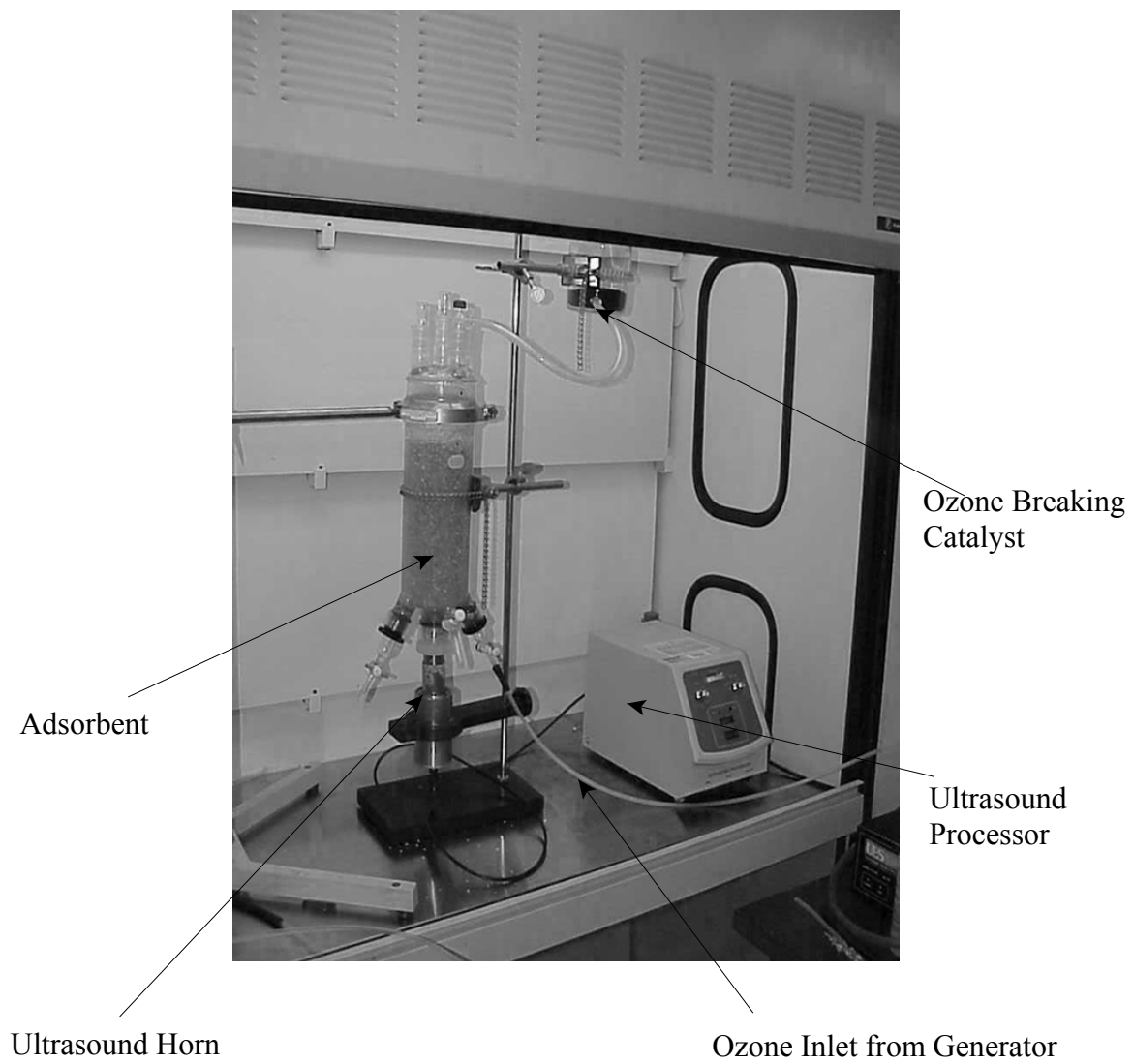
Figure 7.3. Ultrasound-ozonation setup.

# CHAPTER VIII

# INITIAL BATCH STUDIES

This phase of study focused on evaluating the amount of contact time required for the adsorbent to reach adsorption equilibrium with the adsorbate under batch conditions.  To evaluate this contact time, a series of kinetic experiments was conducted. The approximate time when the ratio of equilibrium concentration to initial adsorbate concentration (C/Co) remained almost constant was chosen as the equilibrium time.  All the experiments were run in duplicate.  Raw data for the initial batch studies are given in Appendix A.

Figure 8.1 presents the results for the equilibrium time experiments using kenaf core with 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trinitrotoluene (TNT) as the adsorbates.  It is evident from the figure that 80 % of the adsorption takes place within the first 30 minutes for both TNT and 2,4-DCP.  Based on these data, an equilibrium time of 120 minutes was selected.

The results from the equilibrium time experiments conducted with 2,4-DCP and TNT using kenaf stalk are shown in Figure 8.2.  With these data, over 80% of the adsorption takes place within the first 30 minutes.  An equilibrium time for 2,4-DCP of 120 minutes was selected and an equilibrium time of 60 minutes was selected for TNT.

The results from the equilibrium time experiments using peat moss are shown in

Figure 8.3. Based on these data, an equilibrium time of 120 minutes for TNT adsorption and an equilibrium time of 60 minutes for 2,4-DCP adsorption were selected. As with the other adsorbent, over 80% of the adsorption takes place within the first 30 minutes for peat moss.

The results from the equilibrium time experiments using raw peanut hulls are shown in Figure 8.4. Based on these data, an equilibrium time of 120 minutes was chosen for TNT and 2,4-DCP adsorption.

The results from equilibrium time experiments using crushed peanut hulls are shown in Figure 8.5. Based on these data, an equilibrium time of 60 minutes was chosen for TNT and 180 minutes for 2,4-DCP adsorption.

The results from equilibrium time experiments using hay are shown in Figure 8.6. Based on these data an equilibrium time of 120 minutes was chosen for TNT and 2,4-DCP adsorption.

### **Summary**

Table 8.1 shows the equilibrium time for each adsorbent as determined using TNT and 2,4-DCP as adsorbents. The equilibrium time required for adsorption was found to be between 60 and 180 minutes using 2,4-DCP and between 60 and 120 minutes using TNT as the adsorbate. Obviously, equilibrium time depends on the type of adsorbent and adsorbate used. Also, 80 % of the ultimate adsorption takes place within the first 30 minutes for all the adsorbents, suggesting that the adsorption process is

relatively rapid.  The contact time of the candidate adsorbents are also comparable to granular activated carbon.  A contact time of 2 hours was used for the adsorption of a variety of organics onto granular activated carbon (Dobbs and Cohen, 1980).  The equilibrium times determined were used in all the adsorption isotherm experiments to evaluate the adsorptive capacity of the adsorbents.

Table 8.1. Equilibrium time (minutes) selected for each of the adsorbent.

| Adsorbent | TNT | 2,4-DCP |
|---|---|---|
| Kenaf core | 120 | 120 |
| Kenaf stalk | 60 | 120 |
| Peat moss | 120 | 60 |
| Raw peanut hulls | 120 | 120 |
| Crushed peanut hulls | 60 | 180 |
| Hay | 120 | 120 |
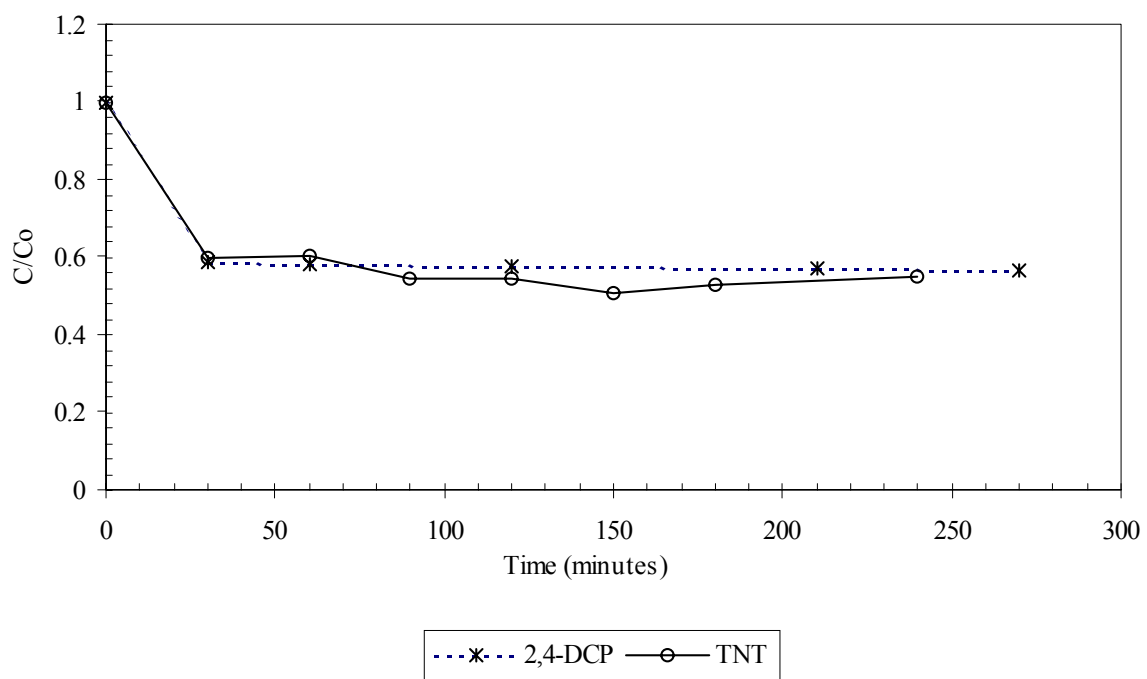
Figure 8.1. Single component equilibrium time experiment plot for kenaf core.
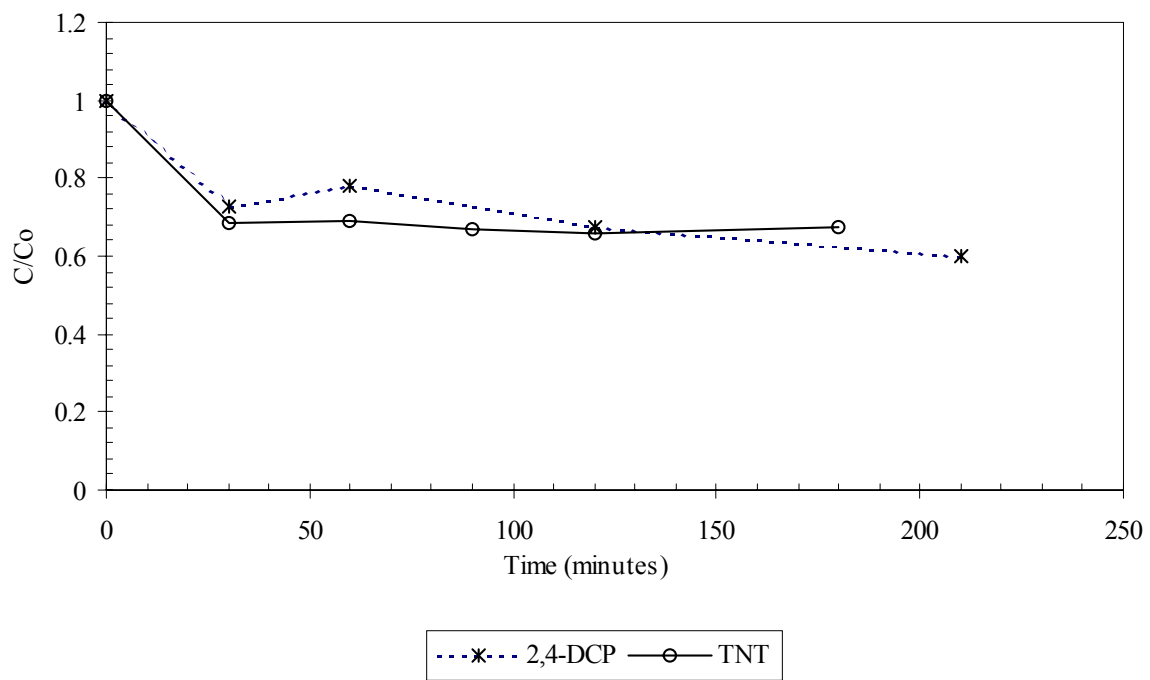
Figure 8.2. Single component equilibrium time experiment plot for kenaf stalk.
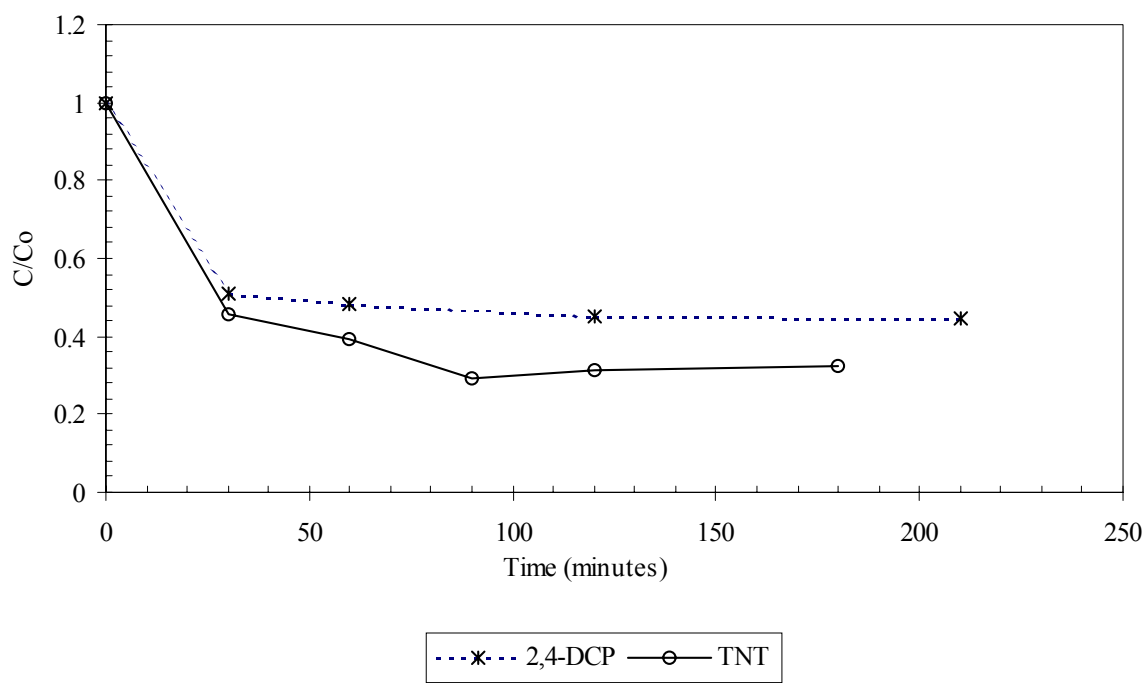
Figure 8.3. Single component equilibrium time experiment plot for peat moss.
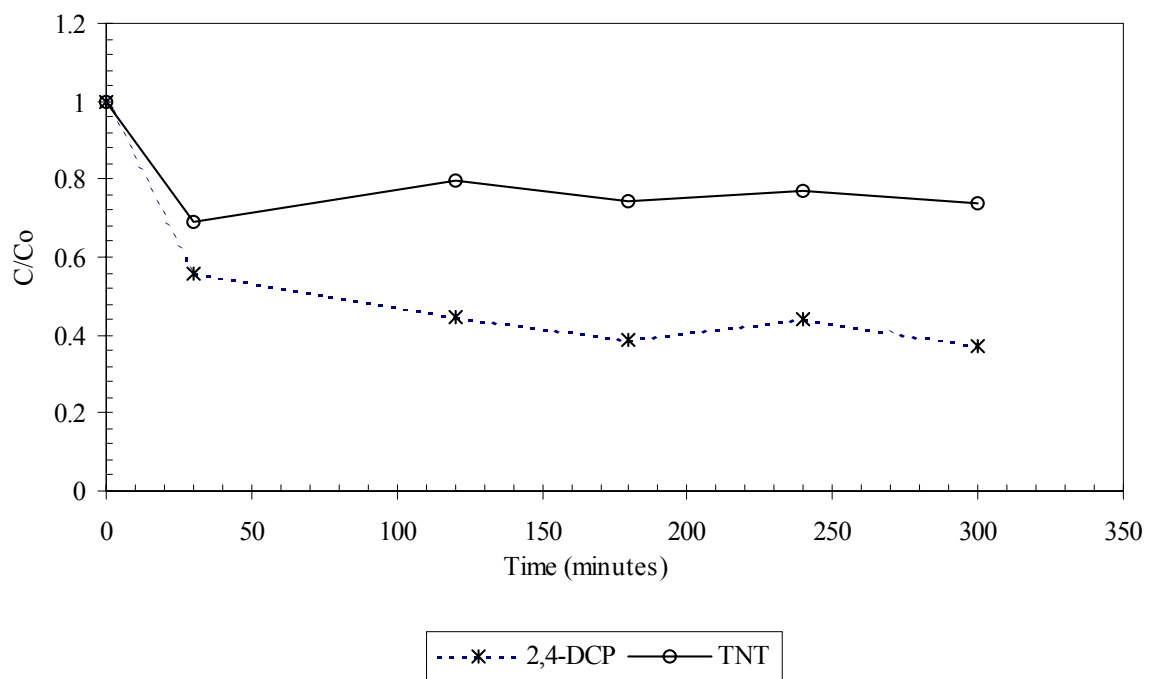
Figure 8.4. Single component equilibrium time experiment plot for raw peanut hulls
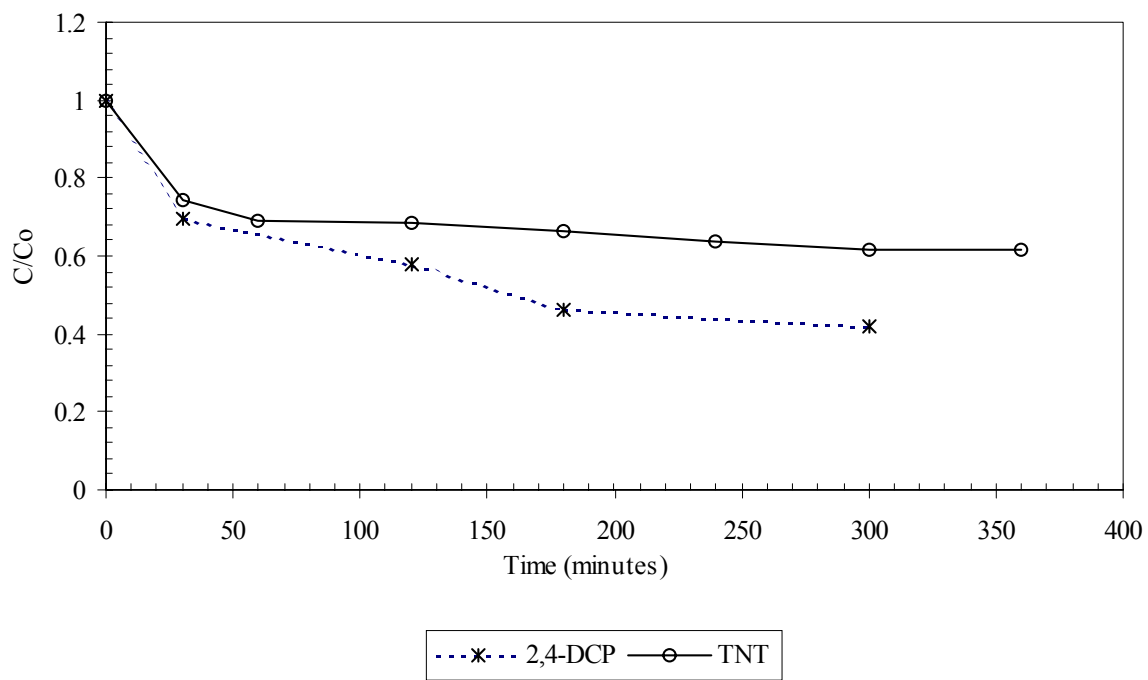
Figure 8.5. Single Component equilibrium time experiment plot for crushed peanut hulls.
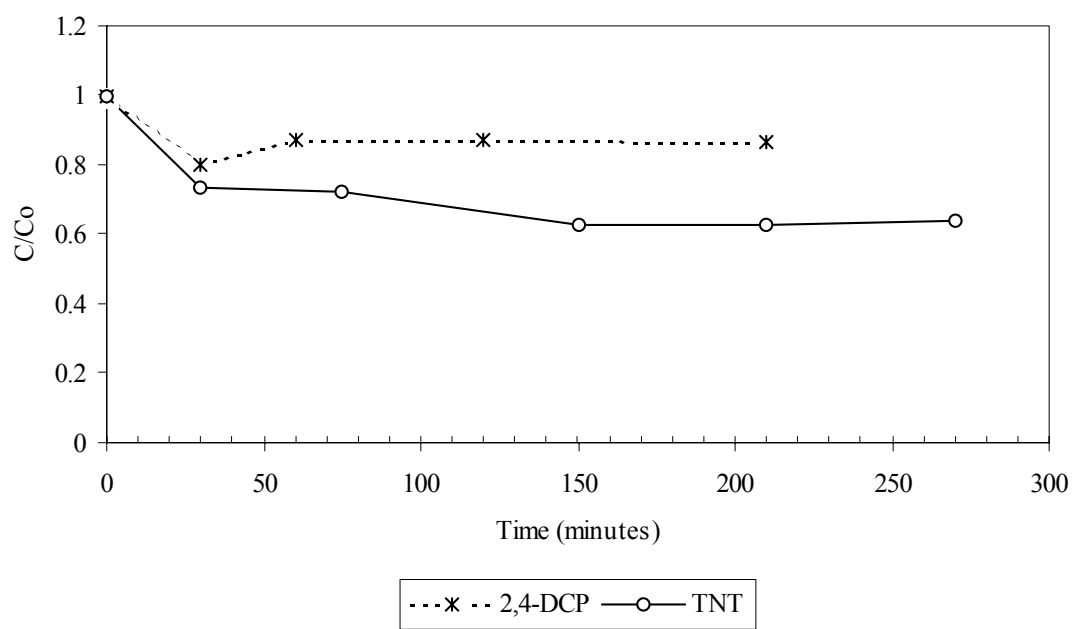
Figure 8.6. Single component equilibrium time experiment plot for hay.

# CHAPTER IX

## EVALUATION OF ADSORPTIVE CAPACITY

This phase of study involved evaluating the adsorptive capacity of each candidate adsorbent for 2,4-DCP and TNT.  Adsorption isotherms were generated and the adsorptive capacity interpreted using the Freundlich Isotherm Model:

$$X/M = kC_f^{1/n} \qquad\qquad (3.2)$$

The constants k and 1/n were obtained by linearly regressing each set of experimental data using the following equation:

$$\log(X/M) = \log(k) + (1/n) \log (C_f) \qquad\qquad (9.2)$$

According to Equation (9.2), a logarithmic plot of X/M against $C_f$ yields a straight line.  The slope is 1/n and the intercept at $C_f = 1$ mg/l is k.  Linear regression analysis was performed on each set of data to calculate the constants and the correlation coefficient for each regression.  Example of an adsorption isotherm is shown in Figure 9.9.

### TNT Adsorption

The Freundlich constants (k and 1/n ) determined from the adsorption isotherms for TNT in water on the candidate adsorbents are shown in Table 9.1.  The values of the correlation coefficient (greater than 0.95) determined for each of the adsorption isotherm indicates that the Freundlich Model adequately fits the experimental data.

The Freundich constants for kenaf core were calculated by regressing two sets of individual isotherm data with initial TNT concentrations of 2 mg/l and 20 mg/l. Three sets of individual isotherms with initial TNT concentrations of 2 mg/l, 20 mg/l, and 40 mg/l were regressed to determine the constants for kenaf stalk. In the case of peat moss, four individual isotherms with initial TNT concentrations of 2 mg/l, 20 mg/l, 40 mg/l, and 70 mg/l were regressed to determine the Freundlich constants. Two sets of individual isotherms with initial TNT concentrations of 20 mg/l and 40 mg/l were regressed to determine the Freundlich constants for TNT adsorption on raw and crushed peanut hulls. The main objective of regressing individual isotherm data is to obtain a single isotherm for each of the candidate adsorbents in adsorbing TNT over a wide concentration range. Adsorption isotherm data and plots are shown in Appendix B and C, respectively.

Table 9.2 shows the adsorption capacities calculated using the Freundlich constants (k and 1/n) at different equilibrium concentrations ($C_f$) of TNT. At equilibrium concentrations of 2 : g/l, 10 : g/l, and 0.5 mg/l of TNT, the adsorption capacity ordering for the natural adsorbents is found to be crushed peanut hulls > peat moss > kenaf stalk > kenaf core > raw peanut hulls (Figures 9.1, 9.2, 9.3). The adsorption capacity ordering is the same for all three equilibrium concentrations studied. Hay did not show any adsorptive capacity and is not compared with other adsorbents. Kenaf core and raw peanut hulls have lower k values when compared to the other candidate adsorbents and as a result they have lower adsorption capacity within the concentration range studied.

Kenaf stalk has intermediate adsorption capacities within the concentration range studied.

Crushed peanut hulls and peat moss have higher k values when compared to the other

candidate adsorbents and as a result the calculated adsorption capacities are higher within

the concentration range studied. The adsorption capacities of the candidate adsorbents

are lower than the adsorption capacity of the two activated carbons (GAC 830 and

Hydrodarco 4000).

### 2,4-DCP Adsorption

The Freundlich constants (k and 1/n) determined from the adsorption isotherms

for 2,4-DCP are shown in Table 9.3. The values of the correlation coefficients (greater

than 0.90) for the regressions indicate that the Freundlich Model adequately fits the

experimental data.

The Freundlich constants for kenaf core, kenaf stalk, and peat moss were obtained

by successfully regressing two sets of individual isotherms with initial concentrations of

5 mg/l and 20 mg/l. Freundlich constants for raw peanut hulls were determined by

regressing isotherm data with 15 mg/l initial 2,4-DCP concentration. The Freundlich

constants for crushed peanut hulls were obtained by regressing individual isotherms with

an initial concentration of 20 mg/l. Adsorption isotherm data and plots are shown in

Appendix B and C, respectively.

Table 9.4 shows the adsorption capacities calculated using the Freundlich

constants (k and 1/n) at different equilibrium concentrations ($C_f$) of 2,4-DCP. At

equilibrium concentrations of 2 : g/l, 10 : g/l, and 0.5 mg/l  of 2,4-DCP, the adsorption

capacity ordering for the candidate adsorbents is found to be raw peanut hulls > peat

moss > kenaf core > kenaf stalk > crushed peanut hulls (Figures 9.4, 9.5, 9.6).  The

adsorption capacity ordering is the same for all three equilibrium concentrations studied.

Raw peanut hulls have the highest adsorption capacity followed by peat moss within the

concentration range studied.  Kenaf core has intermediate adsorption capacity.  Kenaf

stalk and crushed peanut hulls have the lowest adsorption capacities among the candidate

adsorbents within the concentration range studied.  The adsorptive capacity for raw

peanut hulls and peat moss are higher than other candidate adsorbents since they have

higher k values.  Since crushed peanut hulls have a high 1/n value (slope) and a low k

value, the calculated adsorptive capacity are considerably lower than other candidate

adsorbents.  Adsorbents having high slopes will tend to have low adsorption capacity at

lower equilibrium concentration and high adsorption capacity at higher equilibrium

concentration.  Hay did not show any adsorptive capacity and is not compared with other

adsorbents.  The adsorption capacities of the candidate adsorbents are significantly lower

when compared to the adsorption capacity of GAC (Calgon Filtrasorb 300).

The primary reason for the adsorption capacity of the candidate adsorbents to be

lower than GAC could be due to the high surface area of GAC , usually in the range 800 -

1500 $m^2$/g. The BET surface area using nitrogen adsorption for kenaf core was found to

in the range 2.0 - 3.0 $m^2$/g, indicating that superficial surface area is the major source of

adsorption sites for the natural adsorbents.  The BET plot and experimental conditions for

surface area analysis of kenaf core are shown in Appendix C. Since the surface areas of

granular activated carbon and kenaf core are considerably different, the amount (mg) of

TNT adsorbed per square meter of the adsorbent is compared in Figure 9.7. The amount

of TNT adsorbed per square meter of kenaf core is 18 % when compared to that of

Hydrodarco 4000. The mass of 2,4-DCP adsorbed per square meter of the adsorbent is

compared in Figure 9.8. The mass of 2,4-DCP adsorbed per square meter of kenaf core is

33 % when compared to that of Filtrasorb 300. The amount of TNT and 2,4-DCP

adsorbed per unit area of kenaf core is lower when compared to activated carbon. Since

the amount of adsorbate adsorbed per unit area of the adsorbent is different for kenaf core

and GAC, there could be factors such as different pore sizes and presence of different

surface functional groups playing an important role in the adsorption of the test

adsorbates.

## **Summary**

The adsorption isotherms and the calculated adsorption capacities show that the

candidate adsorbents, except hay, possess the ability to remove the test adsorbates from

water. Since the calculated adsorption capacities are based on the Freundlich constants

the adsorptive capacity ordering were found to be different for TNT and 2,4-DCP

adsorption. Crushed peanut hulls had the highest adsorption capacity for TNT within the

equilibrium concentration range studied. Raw peanut hulls had the highest adsorption

capacity for 2,4-DCP within the equilibrium concentration range studied. Hay exhibited

no adsorptive capacity for either adsorbates.  The adsorption capacities of all the

candidate adsorbents were lower than the capacity of GAC for both TNT and 2,4-DCP.

Table 9.1. Freundlich parameters for TNT adsorption.

|  | k (mg/gm)[a] | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| Kenaf core | 0.09 | 0.83 | 0.99 |
| Kenaf stalk | 0.237 | 0.793 | 0.95 |
| Peat moss | 0.230 | 0.684 | 0.99 |
| Raw peanut hulls | 0.03 | 0.902 | 0.97 |
| Crushed peanut hulls | 0.389 | 0.420 | 0.97 |
| GAC 830* | 136 | 0.642 | ng |
| Hydrodarco 4000* | 128 | 0.828 | ng |

a : Adsorption capacity at an equilibrium concentration of 1 mg/l.

* : Wujcik, *et al.,* 1992.

ng : Not given

Table 9.2. Calculated adsorption capacity[b] (mg/gm) at different equilibrium concentrations ($C_f$) of TNT.

| $C_f$ | 2 : g/l | 10 : g/l | 0.5 mg/l |
|---|---|---|---|
| Kenaf Core | 0.0005 | 0.002 | 0.05 |
| Kenaf Stalk | 0.0017 | 0.006 | 0.136 |
| Peat Moss | 0.0032 | 0.009 | 0.143 |
| Raw peanut hulls | 0.00011 | 0.0005 | 0.016 |
| Crushed peanut hulls | 0.0286 | 0.056 | 0.29 |
| GAC 830* | 2.516 | 7.072 | 87.15 |
| Hydrodarco 4000* | 0.745 | 2.826 | 72.10 |

* : Wujcik, *et al.*, 1992

b : Adsorption capacity, $X/M = kC_f^{1/n}$

where,

k, 1/n : Freundlich constants from Table 9.1

$C_f$ : Equilibrium concentration

Table 9.3. Freundlich Parameters for 2,4-DCP adsorption.

|  | k (mg/gm)[a] | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| Kenaf Core | 0.135 | 0.775 | 0.964 |
| Kenaf Stalk | 0.107 | 0.963 | 0.997 |
| Peat Moss | 0.160 | 0.800 | 0.984 |
| Raw Peanut Hulls | 0.321 | 0.560 | 0.9635 |
| Crushed Peanut Hulls | 0.0124 | 1.5 | 0.897 |
| Filtrasorb 300* | 157 | 0.15 | 0.96 |

a : Adsorption capacity at an equilibrium concentration of 1 mg/l.

* : Dobbs and Cohen (1980).

Table 9.4. Calculated adsorption capacity[b] (mg/gm) at different equilibrium concentrations ($C_f$) of 2,4-DCP.

| $C_f$ | 2 : g/l | 10 : g/l | 0.5 mg/l |
|---|---|---|---|
| Kenaf core | 0.00109 | 0.003 | 0.078 |
| Kenaf stalk | 0.00027 | 0.0012 | 0.054 |
| Peat moss | 0.0011 | 0.004 | 0.091 |
| Raw peanut hulls | 0.0098 | 0.024 | 0.217 |
| Crushed peanut hulls | 1.2E-06 | 12.4E-06 | 0.0043 |
| Filtrasorb 300* | 61.81 | 78.68 | 141.5 |

* : Dobbs and Cohen (1980).

b : Adsorption capacity, $X/M = kC_f^{1/n}$

where,

k, 1/n : Freundlich constants from Table 9.3

$C_f$ : Equilibrium concentration
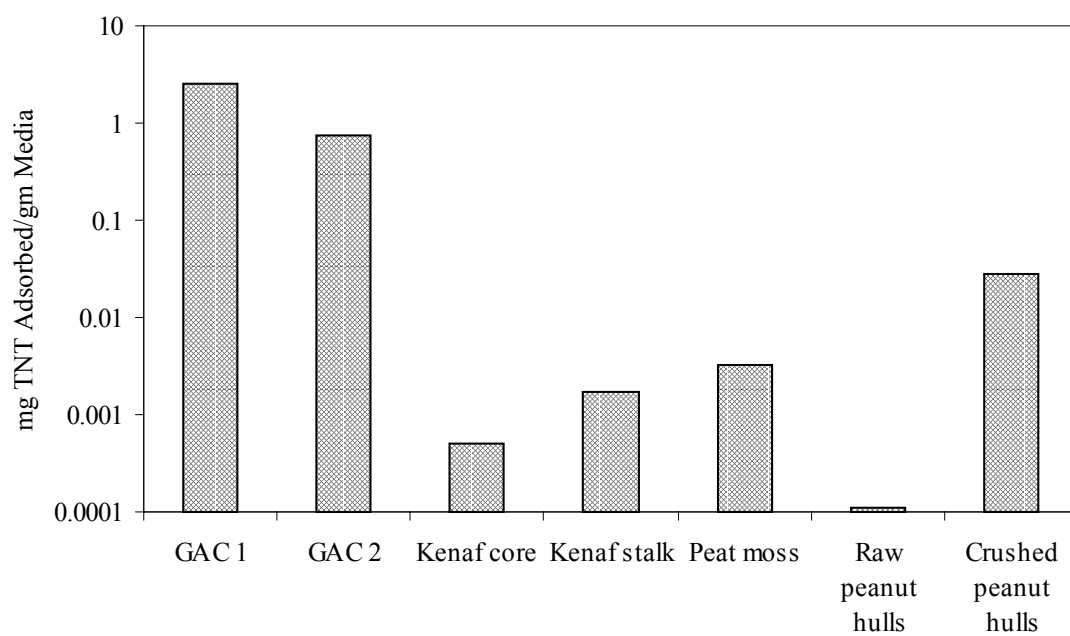
Figure 9.1. Comparison of adsorption capacity at an equilibrium concentration of 2 μg/l of TNT.

GAC 1 : GAC 830 (Wujcik, et al., 1992)
GAC 2 : Hydrodarco 4000 (Wujcik, et al., 1992)
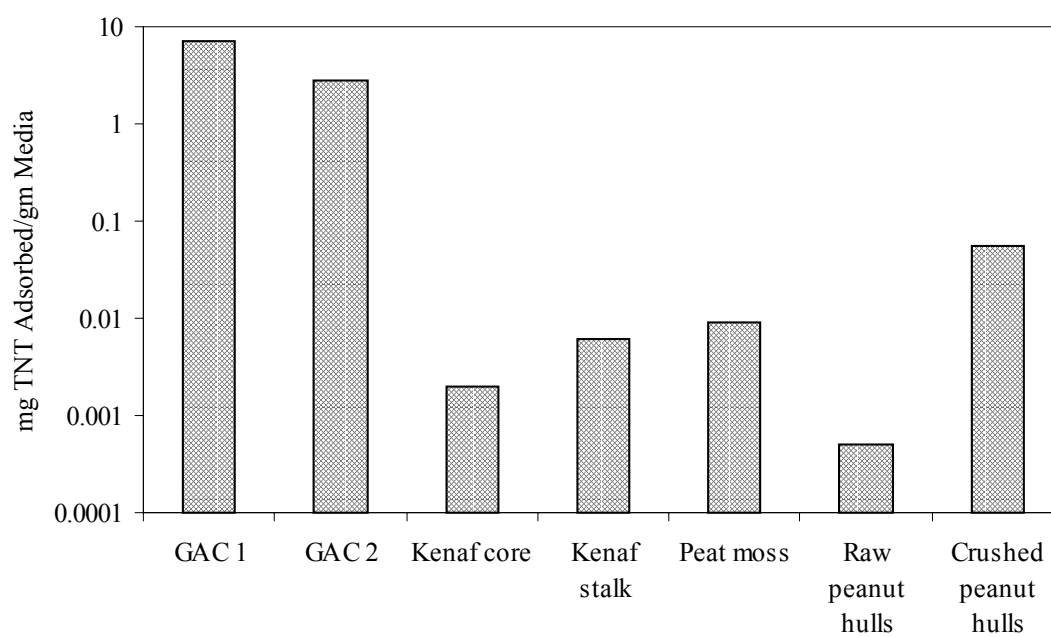
Figure 9.2. Comparison of adsorption capacity at an equilibrium concentration of 10
    : g/l of TNT.

GAC 1: GAC 830 (Wujcik, et al., 1992)
GAC 2: Hydrodarco 4000 (Wujcik, et al., 1992)
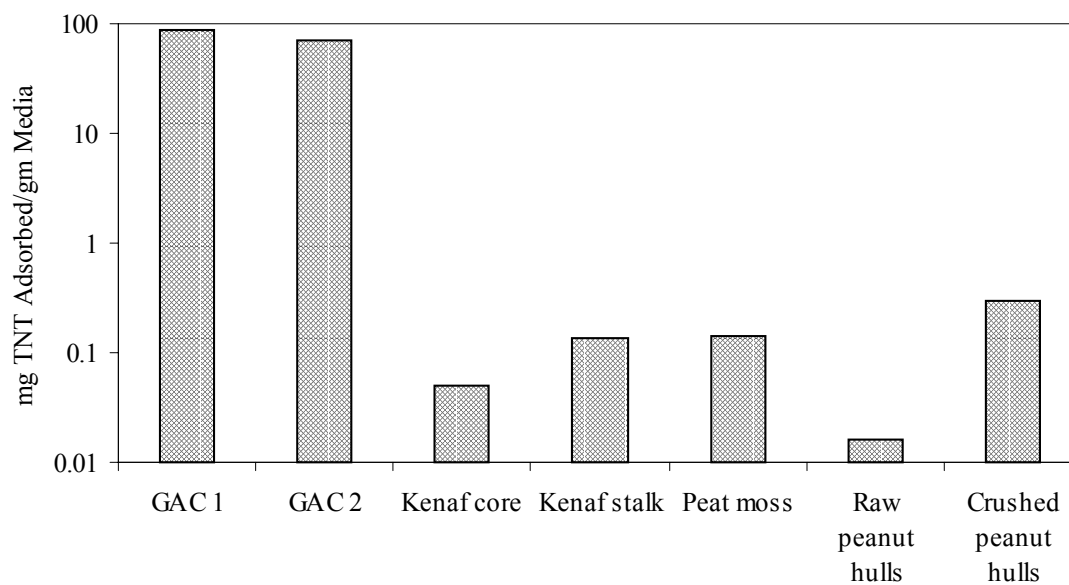
Figure 9.3. Comparison of adsorption capacity at an equilibrium concentration of 0.5 mg/l of TNT.

GAC 1 : GAC 830 (Wujcik, et al., 1992)
GAC 2 : Hydrodarco 4000 (Wujcik, et al., 1992)
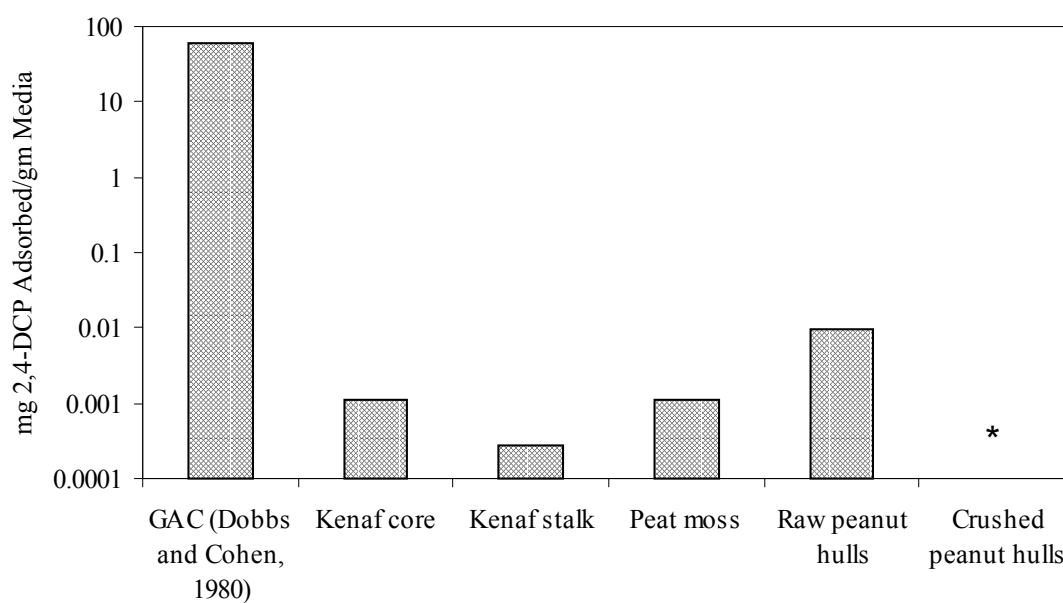
Figure 9.4. Comparison of adsorption capacity at an equilibrium concentration of 2 : g/l of 2,4-DCP.

GAC : Filtrasorb 300
* : No adsorptive capacity
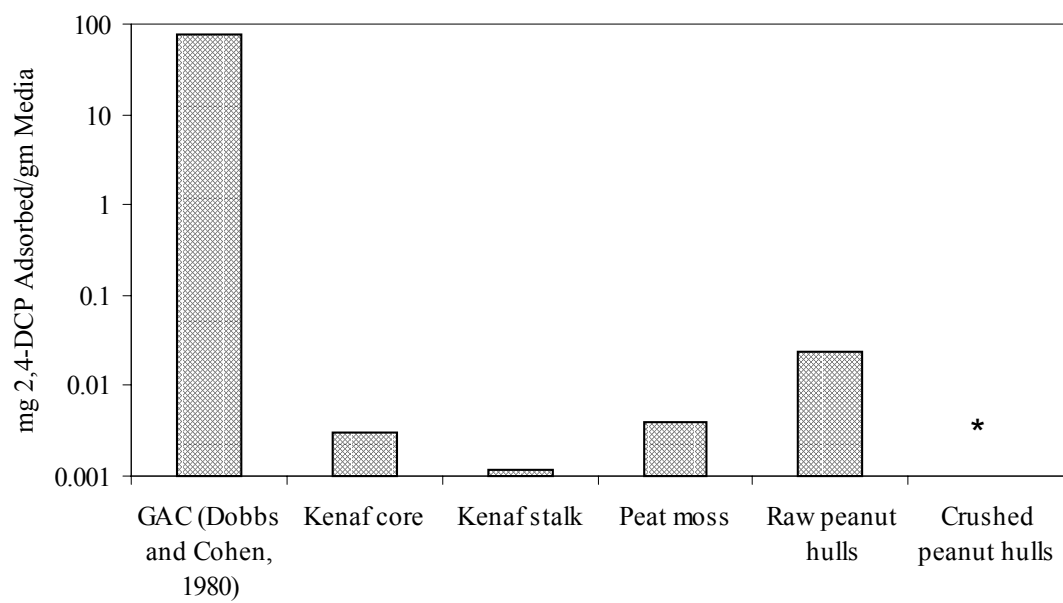
Figure 9.5. Comparison of adsorption capacity at an equilibrium concentration of 10
: g/l of 2,4-DCP

GAC: Filtrasorb 300
* : No adsorptive capacity
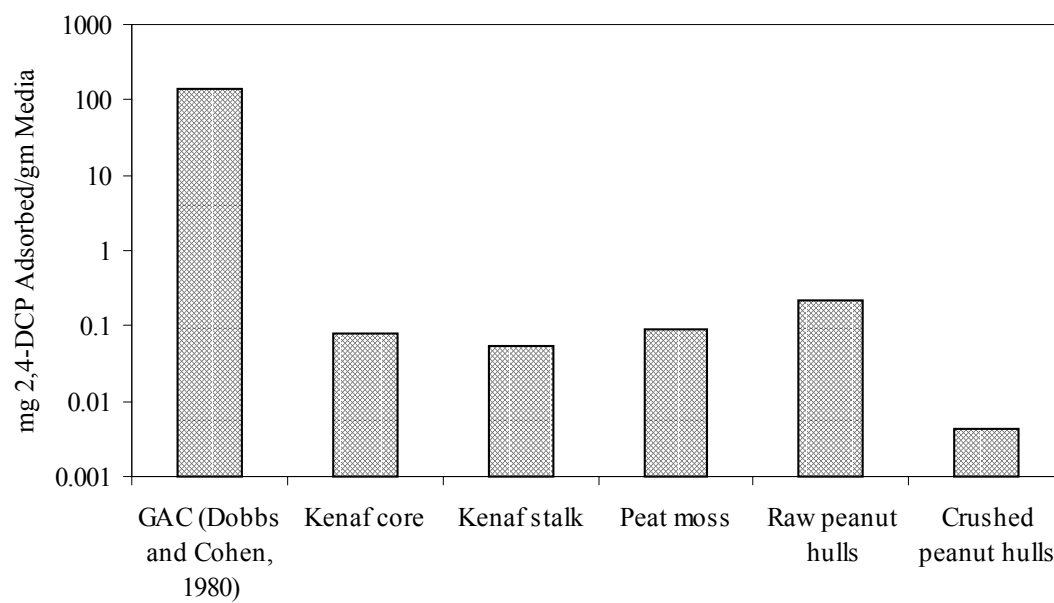
Figure 9.6. Comparison of adsorption capacity at an equilibrium concentration of 0.5 mg/l of 2,4-DCP.

GAC : Filtrasorb 300
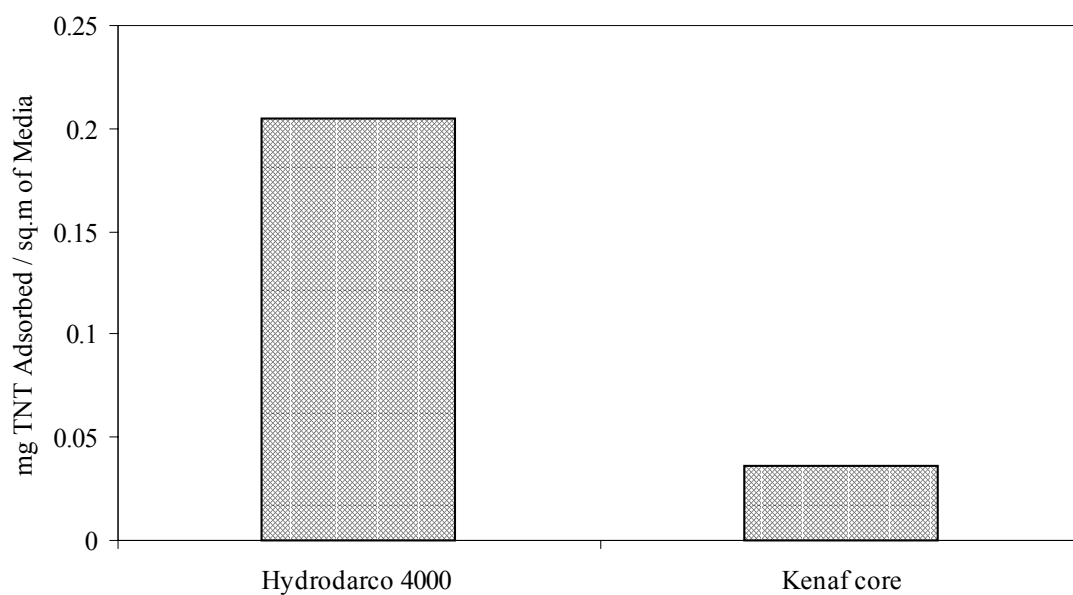
Figure 9.7. Comparison of mass of TNT adsorbed per square meter of the adsorbent at an equilibrium concentration of 1 mg/l.

Note: $\dfrac{\text{mg TNT Adsorbed}}{\text{m}^2 \text{ Media}} = \dfrac{\text{mg TNT Adsorbed / gm Media}}{\text{Surface area of Media (m}^2\text{ / gm)}}$

Surface area of Hydrodarco 4000 = 625 m²/gm (Norit Activated Carbon)
Surface area of kenaf core = 2.5 m²/gm
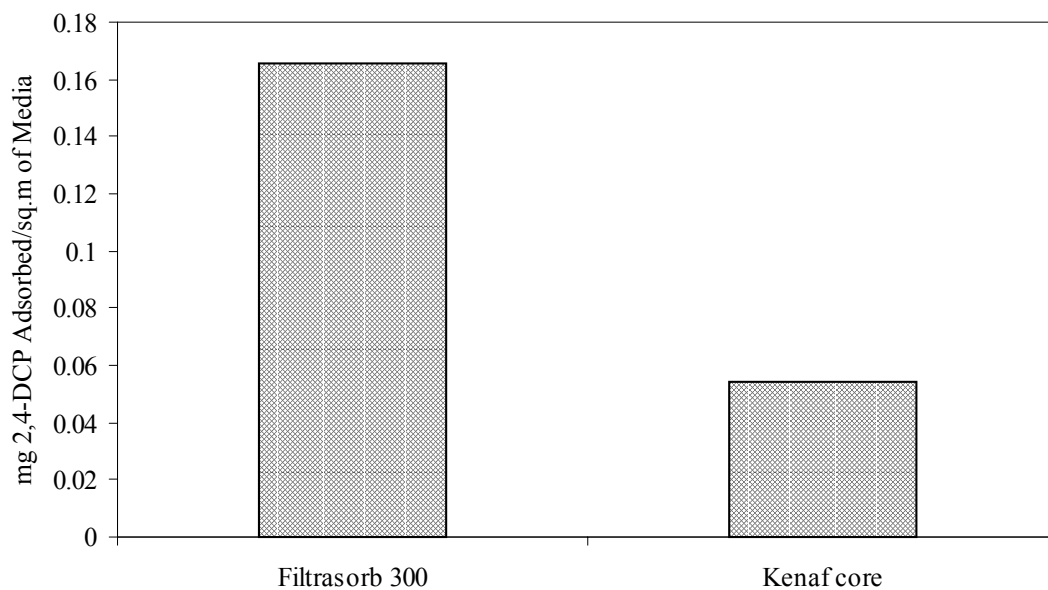
Figure 9.8. Comparison of mass of 2,4-DCP adsorbed per square meter of the adsorbent at an equilibrium concentration of 1mg/l.

Note: $\dfrac{\text{mg 2,4 - DCP Adsorbed}}{\text{m}^2 \text{ Media}} = \dfrac{\text{mg 2,4 - DCP Adsorbed / gm Media}}{\text{Surface area of Media (m}^2 \text{ / gm)}}$

Surface area of Filtrasorb 300 = 950 m$^2$/gm (Calgon Carbon Corp.)
Surface area of kenaf core = 2.5 m$^2$/gm
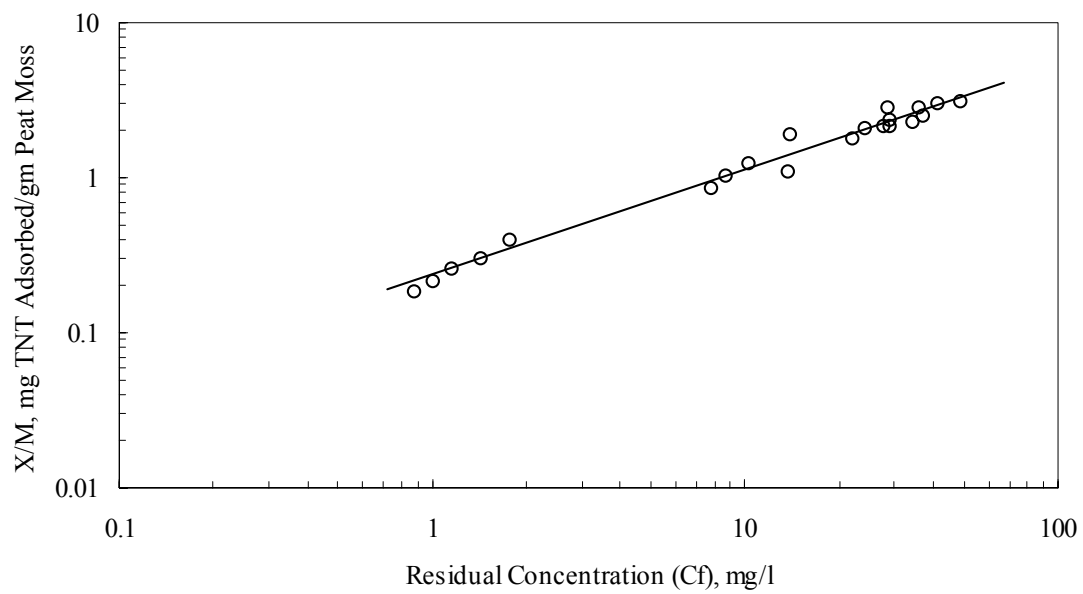
Figure 9.9. Adsorption isotherm plot for peat moss (Temperature = 25 $^0$ C, pH = 5.0)

# CHAPTER X

# EFFECT OF SURFACE OXIDATION ON ADSORPTIVE CAPACITY

## <u>Ozone Pretreatment</u>

Figure 10.1 presents the calculated adsorption capacities of the candidate adsorbents at an equilibrium concentration of 10 : g/l of TNT, before and after ozone pretreatment.  All the isotherm experiments were run in duplicate.  After ozone pretreatment, the adsorption capacities of kenaf core, kenaf stalk, and peat moss were higher when compared to the respective untreated capacity.  For the case of kenaf core the calculated adsorption capacity (0.0112 mg/gm) after pretreatment showed a tremendous increase in magnitude when compared to the untreated capacity (0.00014 mg/gm).  The calculated adsorption capacities for raw and crushed peanut hulls were negligible after pretreatment since the adsorbents exhibited low k values after pretreatment with ozone.  The Freundlich parameters for all the candidate adsorbents before and after pretreatment with ozone is given in Appendix B.

Figure 10.2 presents the calculated adsorption capacities at an equilibrium concentration of 10 mg/l of TNT.  After ozone pretreatment, the adsorption capacities of kenaf stalk, peat moss, raw peanut hulls, and crushed peanut hulls are lower when compared to the untreated capacity.  Kenaf core had the highest adsorption capacity with an equilibrium concentration of 10 mg/l.  The capacity of kenaf core after pretreatment

had a lesser impact when compared to the calculated capacity at an equilibrium

concentration of 10 : g/l.

Figures 10.3 and 10.4 compare the calculated adsorption capacities for the

candidate adsorbents before and after ozone pretreatment at equilibrium concentrations of

10 : g/l and 10 mg/l respectively.  After ozone pretreatment the adsorption capacities of

kenaf core, kenaf stalk, peat moss, and crushed peanut hulls are higher when compared to

the respective untreated  capacity.  Pretreatment had generally increased the adsorption

capacities but there was only a slight increase in magnitude.  Ozonation of raw peanut

hulls had reduced the adsorptive capacity.

**Peroxone Pretreatment**

Figures 10.5 and 10.6 compare the calculated adsorption capacities before and

after peroxone pretreatment at TNT equilibrium concentrations of 10 : g/l and 10 mg/l

respectively.  All the isotherm experiments were run in duplicate The adsorption

capacities of kenaf stalk, peat moss, and crushed peanut hulls were lower after peroxone

pretreatment.  After peroxone pretreatment, kenaf core and raw peanut hulls had lower

capacities when compared to the untreated capacity at an equilibrium concentration of 10

: g/l (Figure 10.5).  At an equilibrium concentration of 10 mg/l (Figure 10.6), kenaf core

and raw peanut hulls showed better adsorption capacities when compared to the untreated

adsorbent's capacity since the 1/n values were higher after pretreatment. The Freundlich

parameters for all the candidate adsorbents before and after pretreatment with peroxone is

given in Appendix B.

Figures 10.7 and 10.8 compare the adsorption capacities before and after peroxone pretreatment at 2,4-DCP equilibrium concentrations of 10 : g/l and 10 mg/l. After peroxone pretreatment, the adsorption capacities of kenaf stalk, raw peanut hulls, and crushed peanut hulls are lower at both the equilibrium concentrations. The adsorption capacity of peat moss had increased after pretreatment at both the equilibrium concentrations. Kenaf core depicts lower adsorption capacity when compared to untreated kenaf core at an equilibrium concentration of 10 : g/l (Figure 10.7) but had higher adsorption capacity after peroxone pretreatment at an equilibrium concentration of 10 mg/l.

## **Ultrasound and Ozone Pretreatment**

Figures 10.9 and 10.10 compare the adsorption capacities before and after pretreatment with ultrasound and ozone at TNT equilibrium concentrations of 10 : g/l and 10 mg/l. All the isotherm experiments were run in duplicate Peat moss shows a reduction in adsorption capacity after pretreatment for 10 : g/l and 10 mg/l equilibrium concentrations. Raw peanut hulls show an increase in adsorption capacity after pretreatment at 10 : g/l and 10 mg/l equilibrium concentrations. Kenaf core shows a reduction in adsorption capacity at 10 : g/l (Figure 10.9) but the capacity after pretreatment seems to increase when compared to untreated capacity at an equilibrium concentration of 10 mg/l. The Freundlich parameters for all the candidate adsorbents

before and after pretreatment with ultrasound and ozone is given in Appendix B.

Figures 10.11 and 10.12 compare the adsorption capacities before and after pretreatment at 2,4-DCP equilibrium concentrations of 10 : g/l and 10 mg/l.  Raw peanut hulls show a reduction in adsorption capacity after pretreatment at 10 : g/l and 10 mg/l equilibrium concentrations.  Kenaf core showed an increase in adsorption capacity after pretreatment within the equilibrium concentrations studied.  Peat moss showed a reduction in adsorption capacity at 10 : g/l (Figure 10.9) but the capacity after pretreatment seems to increase when compared to untreated peat moss capacity at an equilibrium concentration of 10 mg/l.

## Discussion

Surface oxidation of the candidate adsorbents was carried out to study its effect on the adsorptive capacity for TNT and 2,4-DCP adsorption.  It was found that the adsorptive capacity of kenaf core was enhanced by all three surface oxidation techniques studied.  The adsorptive capacity of other candidate adsorbents varied with the type of oxidation technique used.  Ozonation showed a greater increase in the magnitude of the adsorption capacity when compared to peroxone and the combination of ultrasound and ozone within the concentration range studied.  The higher increase in adsorptive capacity magnitude following ozonation could be due to the selective oxidation of the adsorbent surface.  Selective oxidation of the adsorbent surface could mean that only certain areas of the adsorbent surface have been oxidised.  Peroxone and combination of ultrasound

and ozone are hydroxyl radical driven and are non-selective when oxidizing the

adsorbent surface. Also, ultrasound can cause a washing effect on the adsorbent surface,

which also could have been the reason for lesser magnitude increase in adsorption

capacity when compared to ozonation. The surface oxidation techniques might have

increased the number of active surface functional groups on the adsorbent surface. This

increase in surface functional groups is dependent on the type of organic groups available

on the adsorbent surface and the oxidizer type. The type of surface functional groups

may vary with the candidate adsorbents. It should be noted that the type of surface

functional groups (acidic, basic, or neutral) before and after pretreatment were not

determined in this study; therefore, the actual reason for the observed changes in

adsorptive capacity cannot be fully determined from this study.
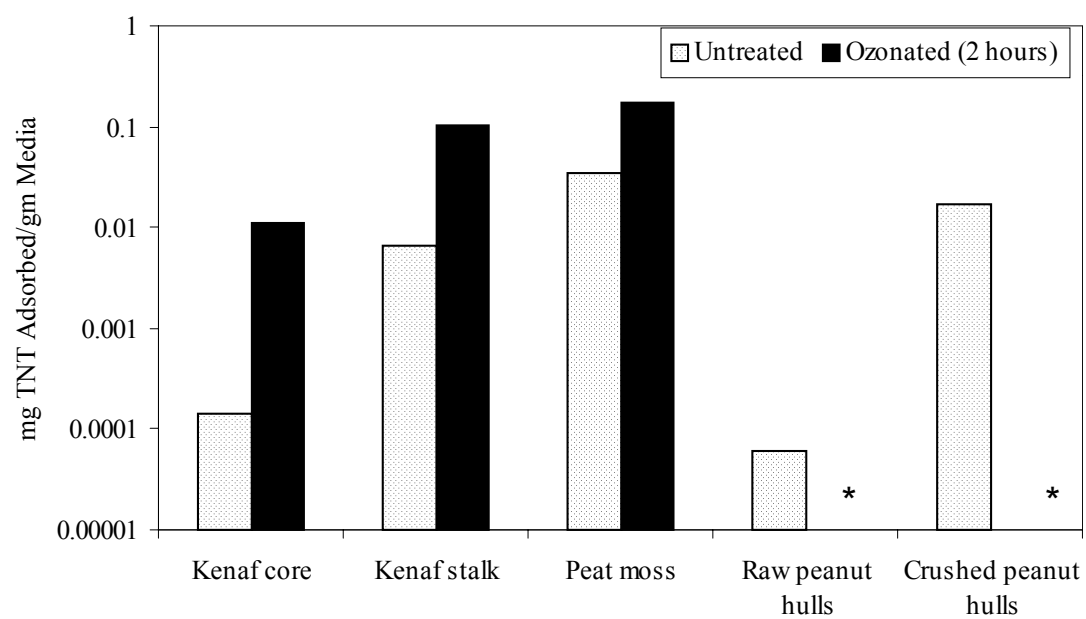
Figure 10.1. Effect of ozone pretreatment on TNT adsorption using an equilibrium
concentration of 10 : g/l.

* : No adsorption capacity.
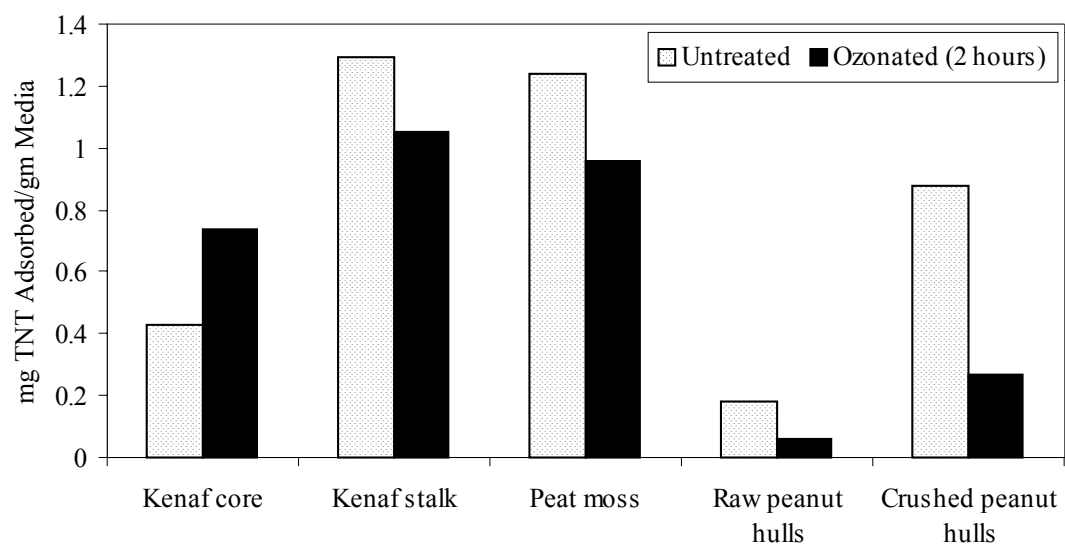
Figure 10.2. Effect of ozone pretreatment on TNT adsorption at using an equilibrium concentration of 10 mg/l.
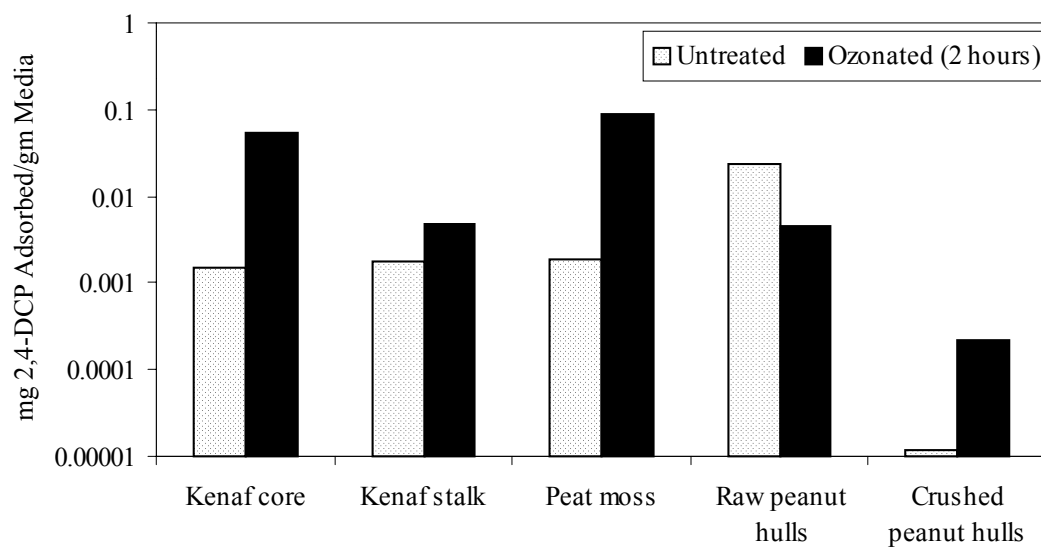
Figure 10.3. Effect of ozone pretreatment on 2,4-DCP adsorption using an equilibrium concentration of 10 : g/l.
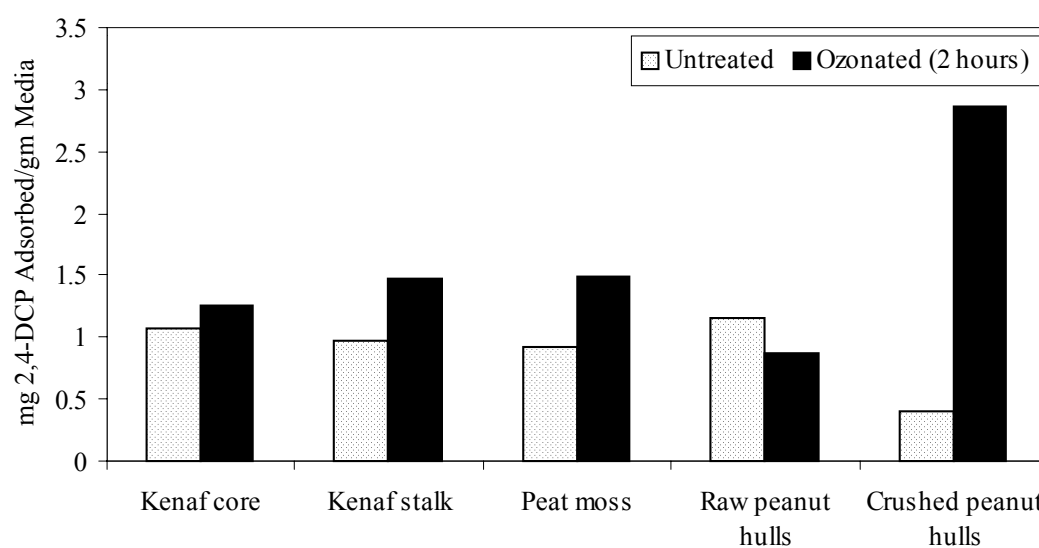
Figure 10.4. Effect of ozone pretreatment on 2,4-DCP adsorption using an equilibrium concentration of 10 mg/l.
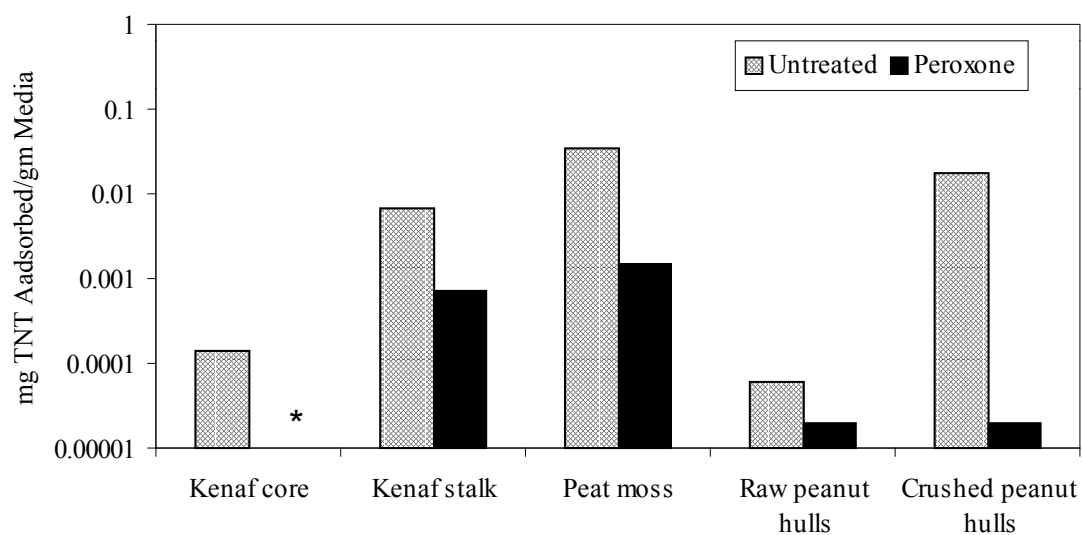
Figure 10.5. Effect of peroxone pretreatment on TNT adsorption using an equilibrium
concentration of 10 : g/l.

* : No adsorption capacity.
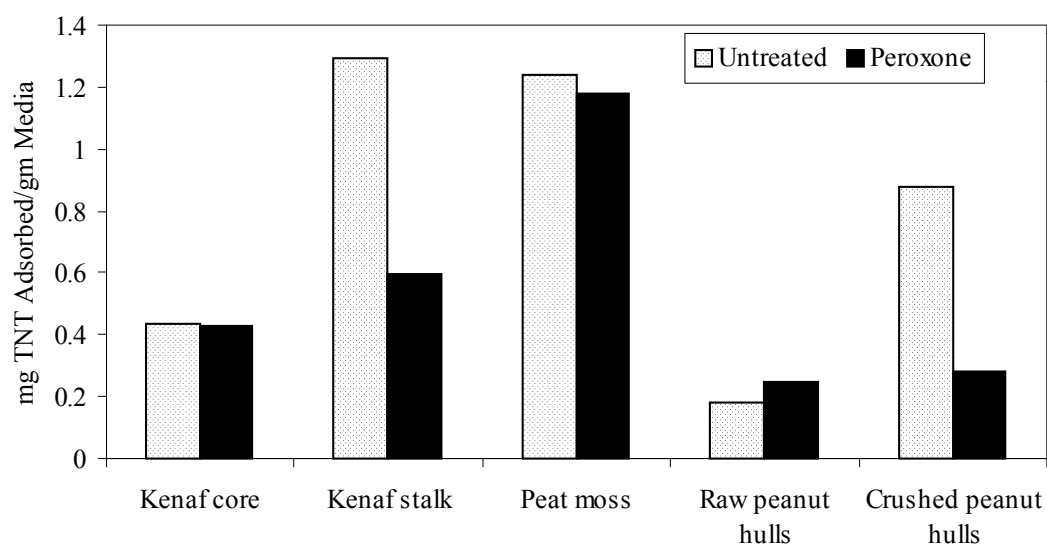
Figure 10.6. Effect of peroxone pretreatment on TNT adsorption at an equilibrium
concentration of 10 mg/l.
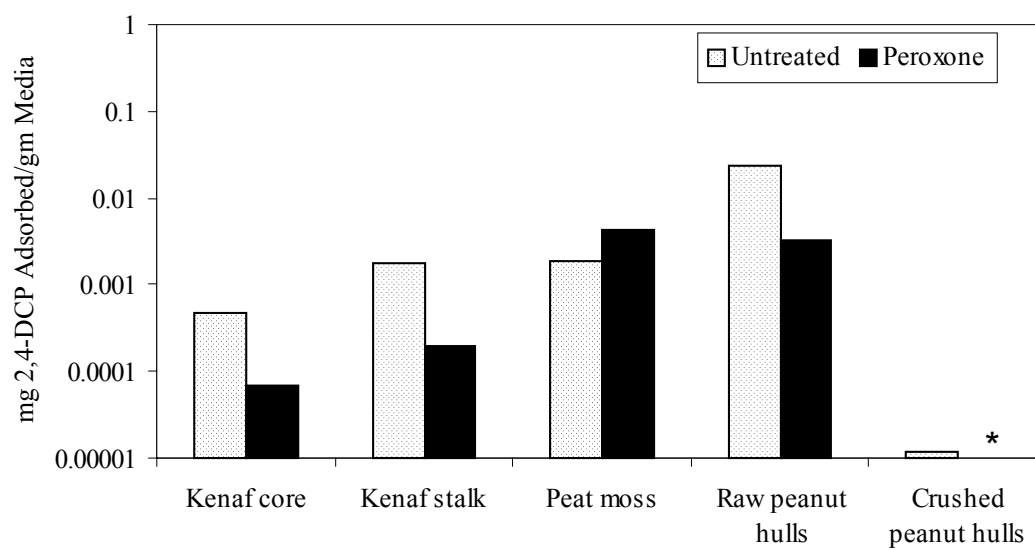
Figure 10.7. Effect of peroxone pretreatment on 2,4-DCP adsorption using an equilibrium concentration of 10 : g/l.

* : No adsorption capacity.
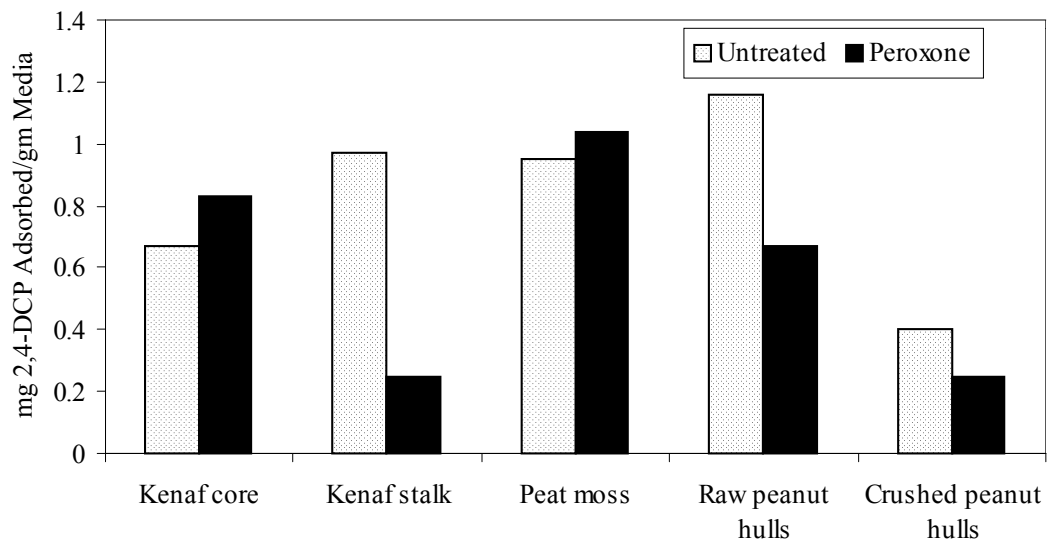
Figure 10.8. Effect of peroxone pretreatment on 2,4-DCP adsorption using an equilibrium concentration of 10 mg/l.
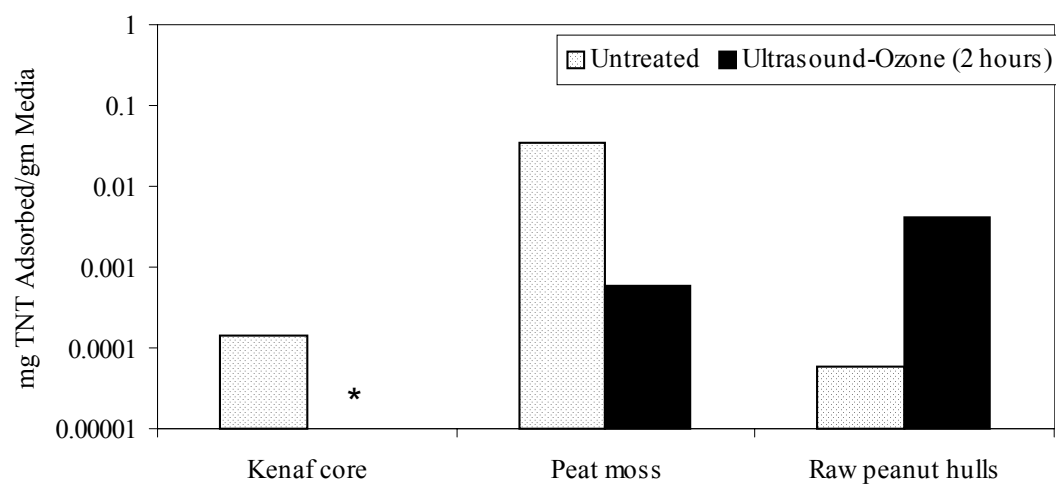
Figure 10.9. Effect of combination of ultrasound and ozone on TNT adsorption using an equilibrium concentration of 10 : g/l.

* : No adsorption capacity.
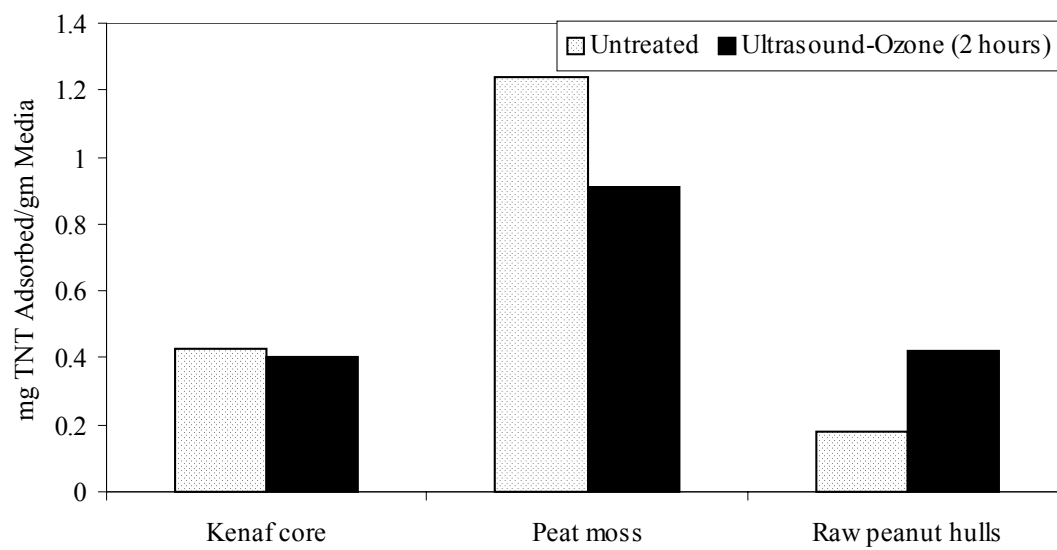
Figure 10.10. Effect of combination of ultrasound and ozone on TNT adsorption using an equilibrium concentration of 10 mg/l.
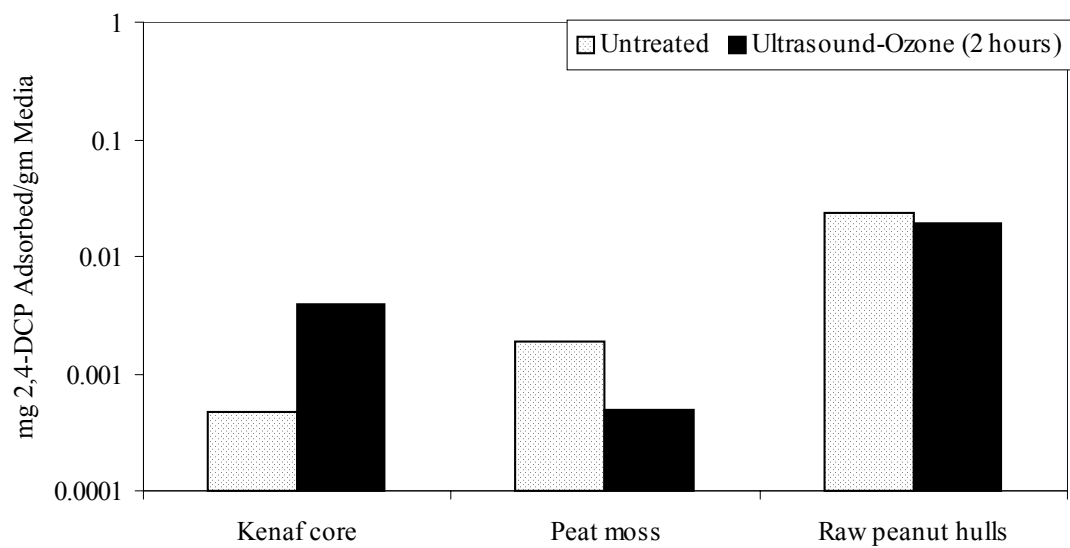
Figure 10.11. Effect of combination of ultrasound and ozone on 2,4-DCP adsorption at an equilibrium concentration of 10 : g/l.
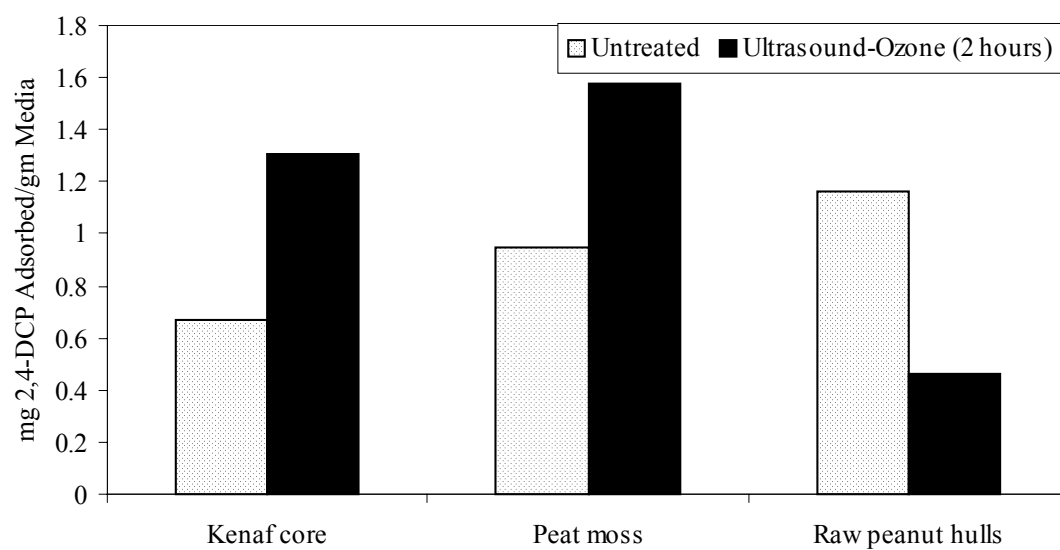
Figure 10.12. Effect of combination of ultrasound and ozone on 2,4-DCP adsorption at an equilibrium concentration of 10 mg/l.

# CHAPTER XI

# DYNAMIC COLUMN STUDIES

The theoretical adsorption capacity of an adsorbent at any final concentration can

be calculated by making use of the Freundlich constants (k and 1/n) and using the

Freundlich Model (Dobbs and Cohen, 1980).  The value of the adsorptive capacity thus

obtained represents the amount of adsorbate adsorbed per unit weight of the adsorbent

when the effluent concentration is equal to the influent concentration (Dobbs and Cohen,

1980; Metcalf and Eddy, 1991; Wujcik *et al.*, 1992).  Influent 2,4-DCP concentration of

about 80 mg/l was used for all the column experiments. The adsorption capacity during

continuous column operation can be estimated by making use of the breakthrough curve.

Breakthrough being defined as the point when a specified amount of the influent is

detected in the effluent (LaGrega et al., 1994).  A breakthrough of 10 % occurs when the

concentration of the effluent is 10 % of the influent concentration and 90 % breakthrough

occurs when the concentration of the effluent is 90 % of the influent concentration.  The

area between the ordinate and the breakthrough curve gives the concentration of the

adsorbate removed over the test time.  The amount of adsorbate removed per gram of

adsorbent is then obtained by dividing the total amount of adsorbate removed by the mass

of the adsorbent in the column.

Continuous flow studies were performed to compare the adsorption capacity

obtained from a continuous column experiment to those determined from batch testing. 2,4-DCP was used as the adsorbate in these experiments. Kenaf core, kenaf stalk, and raw peanut hulls were used for this experimental phase since they had the highest adsorption capacity for 2,4-DCP as determined from the isotherm experiments (Chapter IX).

## **Empty Bed Contact Time**

Empty Bed Contact Time (EBCT) is the time a fluid spends in the column, on the basis that the column is empty (Cooney, 1999). EBCT can be defined as follows,

$$\text{EBCT(min)} = \frac{\text{Bed Volume (l)}}{\text{Volumetric flowrate (l/min)}} \qquad (11.1)$$

Thus, using flows of 0.01 l/min and 0.028 l/min yielded empty bed contact times of 20 and 60 minutes. The bed volume was 0.6 l for this study.

The breakthrough times for kenaf core, kenaf stalk, and raw peanut hulls at 20 and 60 minutes EBCT are shown in Tables 11.1 and 11.2, respectively. The continuous column studies data are shown in Appendix D and the breakthrough curves are shown in Appendix E. It is to be noted that the column studies were not done in duplicate. The initial breakthrough (10 %) times for kenaf core are considerably higher than kenaf stalk and raw peanut hulls for both the contact times studied. This means that kenaf core has the ability of retaining the adsorbate within the column more efficiently than the other two candidate adsorbents. The reason for initial breakthrough to occur earlier for kenaf

stalk and raw peanut hulls could be due more void volume in the adsorbent bed.  The breakthrough times are higher when higher contact times were used. This is due to the fact that there is more of contact time available for the adsorbent to attain equilibrium with the adsorbate.

Tables 11.3 compares theoretical adsorption capacity (determined using the Freundich Model parameters) to actual adsorption capacity obtained during continuous column operation.  The theoretical and breakthrough (actual) capacity were calculated at 90 % breakthrough of the initial adsorbate concentration. Kenaf core has the highest adsorption capacity among the candidate adsorbents studied. The capacity of kenaf core was also found to be slightly greater than the theoretical capacity calculated using batch adsorption data.  The capacity of raw peanut hulls was 90 % of the theoretical capacity. This means that 20 minutes of contact time would be adequate for kenaf core and raw peanut hulls to adsorb 2,4-DCP during continuous column operation.  The capacity of kenaf stalk during continuous column operation was 65 % of the theoretical capacity. Thus, higher contact times are necessary for kenaf stalk to achieve its maximum capacity during continuous column operation.  When compared to granular activated carbon, kenaf stalk appears to require more contact time.  The contact times for kenaf core and raw peanut hulls are comparable to the contact times used for GAC. Generally, contact times ranging from 15 to 40 minutes are used for granular activated carbon for adsorbing organics (USEPA, 1973).

Table 11.1. Breakthrough time (minutes) at an EBCT of 20 minutes.

| Adsorbent | 10 % Breakthrough | Complete Breakthrough |
|---|---|---|
| Kenaf core | 48 min | 720 min |
| Kenaf stalk | 6min | 300 min |
| Raw peanut hulls | 12 min | 660 min |

Table 11.2. Breakthrough time (minutes) at an EBCT of 60 minutes.

| Adsorbent | 10 % Breakthrough | Complete Breakthrough |
|---|---|---|
| Kenaf core | 168 min | 1500 min |
| Kenaf stalk | 18 min | 1620 min |
| Raw peanut hulls | 18 min | 1260 min |

Table 11.3. Comparison of theoretical and breakthrough adsorption capacity at 90 % of initial 2,4-DCP concentration. Contact time = 20 minutes.

| Adsorbent | Theoretical Capacity, mg/gm[a] | Actual Capacity, mg/gm[b] | %) [c] |
|---|---|---|---|
| Kenaf core | 3.838 | 4.5 | 114 % |
| Kenaf stalk | 6.195 | 3.92 | 64 % |
| Raw peanut hulls | 3.192 | 2.92 | 91 % |

a: Theoretical adsorption capacity, calculated using isotherm data.

b: Calculated from breakthrough curve,

Actual capacity = (A x Q)/M$_c$
where,

A = Area between ordinate and breakthrough curve, $\dfrac{mg.hr}{l}$

Q = Flow rate, l/hr

M$_c$ = Mass of adsorbent in column, gm.

c: Percentage of theoretical adsorption capacity.

# CHAPTER XII

## ADSORBENT REQUIREMENTS AND COST

Adsorbent requirements for column operation can be estimated by using the

Freundlich Isotherm Model (Dobbs and Cohen, 1980). To estimate the adsorbent

requirements, the adsorption capacity is obtained from the isotherm plot or by using the

Frendlich constants (k and 1/n) in the Freundlich Model for the concentration of the

adsorbate to be treated. The adsorption capacity thus obtained is the ultimate capacity

$(X/M)_{Co}$ of the adsorbent for the adsorbate at that concentration (Co). This capacity is the

maximum loading attainable during column operation for a single component influent,

when the column is operated until the adsorbate concentration is the same in the influent

and effluent. The adsorbent requirement was based on the ultimate capacity and was

calculated using the following formula (Dobbs and Cohen, 1980) :

$$\text{Adsorbent Requirement} = \frac{Co}{\left(\dfrac{X}{M}\right)_{Co}} \qquad (12.1)$$

where,

Adsorbent requirement = g of adsorbent required/l of influent

Co = Influent initial concentration, mg/l

$(X/M)_{Co}$ = Ultimate capacity of the adsorbent, mg/gm

The adsorbent costs can be estimated once adsorbent requirements are known. The costs are based on only the adsorbent requirement costs at saturation capacity for all the candidate adsorbents and does not include capital, operational, and handling. The costs after ozone pretreatment is compared only for kenaf core, since surface oxidation enhanced the adsorptive capacity of kenaf core for both TNT and 2,4-DCP adsorption (Chapter X). It was assumed that the cost of ozonation was 10 % of the cost of the untreated adsorbent. It was also assumed that the costs of raw and crushed peanut hulls are the same.

Table 12.1 shows the adsorbent requirement cost ($/gal) for TNT adsorption based on the adsorption capacity and the cost of the adsorbent. Figure 12.1 shows a comparison of adsorbent requirement costs for TNT at 500 : g/l influent concentration. Influent of 500 : g/l was the average concentration of TNT found at Milan Army Ammunition Plant (MAAP) in Milan, Tennessee (Wujcik, et al., 1992). Thus, the influent concentration for TNT contaminated wastewater stream was assumed to be 500 : g/l. The adsorbent cost requirements associated with crushed peanut hulls and kenaf stalk is competitive when compared to Granular Activated Carbon (GAC) costs. The costs associated with kenaf core (untreated and ozonated), peat moss, and raw peanut hulls are the highest among the candidate adsorbents and are also higher than GAC. Though the cost of raw peanut hulls are lower than other candidate adsorbents ($0.007/lb) the adsorbent requirement cost for raw peanut hulls is high since the

adsorptive capacity for TNT adsorption is very low (Chapter IX). The adsorbent

requirement cost of ozonated kenaf core is 50 % lower than the untreated kenaf core

requirement cost since the adsorptive capacity after ozone pretreament is considerably

higher than the untreated capacity (Chapter X).

Table 12.2 shows the adsorbent requirement cost ($/gal) for 2,4-DCP adsorption

based on the adsorption capacity and the cost of the adsorbent. Figure 12.2 shows a

comparison of adsorbent requirement costs for treating a 5 mg/l of 2,4-DCP influent at

saturation capacity. The adsorbent cost requirements associated with raw peanut hulls

and kenaf stalk are competitive when compared to Granular Activated Carbon (GAC)

costs. The costs associated with kenaf core (untreated and ozonated), peat moss, and

crushed peanut hulls are the highest among the candidate adsorbents and are also higher

than GAC.

Tables 12.3 and 12.4 show the calculated adsorbent bed volume required on a

daily basis with the plant operating with a flow rate of 100 gpm. The bed volume

required by the candidate adsorbents are higher than GAC, meaning larger adsorption

contactors would be required when using the candidate adsorbents. It should be noted

that the bed volume required by ozonated kenaf core is only 50 % of the volume required

by untreated kenaf core. The drawbacks associated with larger bed volumes using the

candidate adsorbents could be reduced since there is a possibility of densification of the

candidate adsorbents. By densifying the candidate adsorbents, the bed volumes could be

reduced by at least 4 times without crushing the adsorbent (Zappi, 2000). GAC cannot

be compressed to reduce the bed volume as it gets crushed into useless fines under high

impact (Zappi, 2000).

Table 12.1. Adsorbent requirement costs for TNT adsorption at saturation capacity. Influent concentration = 500 : g/l.

| Adsorbent | (X/M)co, mg/gm | Adsorbent Requirement [b], lb/gal | Adsorbent Cost, $/lb | Adsorbent Requirement Cost, $/gal |
|---|---|---|---|---|
| Kenaf core | 0.0526 | 0.0790 | 0.12 | 0.0095 |
| Ozonated kenaf core | 0.120 | 0.0344 | 0.132 | 0.0045 |
| Kenaf stalk | 0.1367 | 0.0304 | 0.005 | 0.0001 |
| Peat moss | 0.1431 | 0.0290 | 0.375 | 0.0110 |
| Raw peanut hulls | 0.0160 | 0.2594 | 0.007[d] | 0.0018 |
| Crushed peanut hulls | 0.2907 | 0.0143 | 0.007 | 0.0001 |
| GAC | 72.1036 [a] | 5.77641E-05 | 2 | 0.0001 |

a : Adsorption capacity for Hydrodarco 4000 (Wujcik, et al., 1992).

Table 12.2. Adsorbent requirement costs for 2,4-DCP adsorption at saturation capacity. Influent concentration = 5 mg/l.

| Adsorbent | (X/M)co, mg/gm | Adsorbent Requirement [b], lb/gal | Adsorbent Cost, $/lb | Adsorbent Requirement Cost, $/gal |
|---|---|---|---|---|
| Kenaf core | 0.46993 | 0.08862 | 0.12 | 0.0106 |
| Ozonated kenaf core | 0.922 | 0.045 | 0.132 | 0.006 |
| Kenaf stalk | 0.50407 | 0.08262 | 0.005 | 0.0004 |
| Peat moss | 0.57982 | 0.07183 | 0.375 | 0.0269 |
| Raw peanut hulls | 0.79054 | 0.05268 | 0.007[d] | 0.0003 |
| Crushed peanut hulls | 0.13863 | 0.30042 | 0.007 | 0.0021 |
| GAC | 199.868 [c] | 0.00020 | 2 | 0.0004 |

b : Calculated using formula 12.1 (Dobbs and Cohen, 1980).

c : Adsorption capacity for Filtrasorb 300 (Dobbs and Cohen, 1980).

d: Brown, et al., 2000.
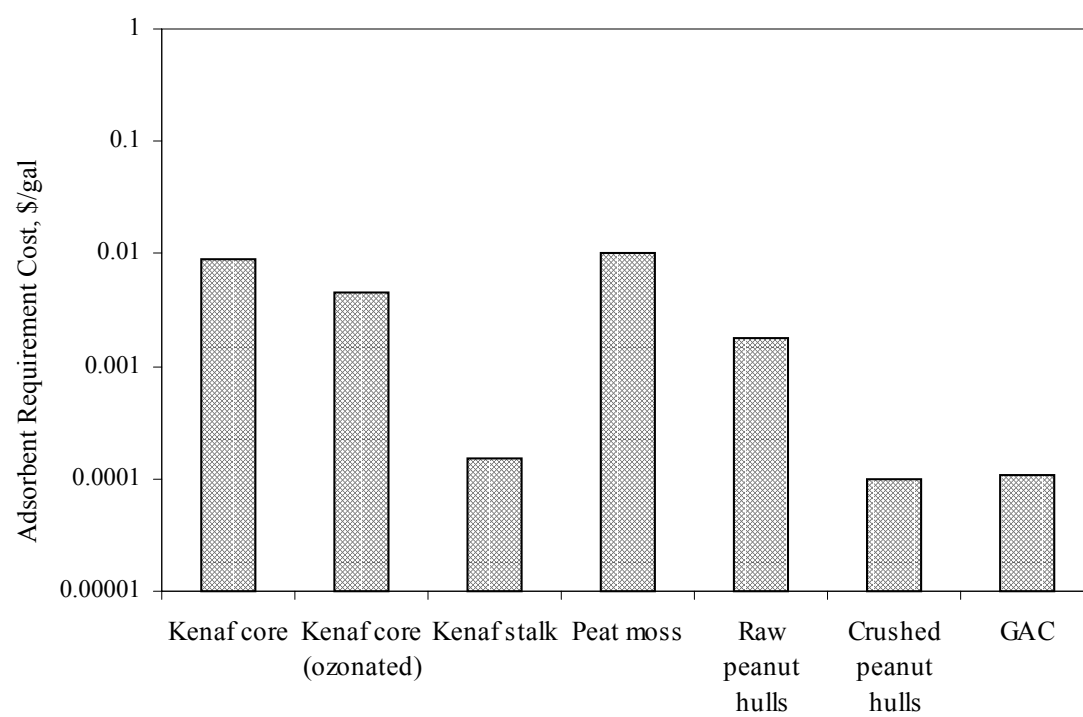
Figure 12.1. Comparison of adsorbent requirement cost for treating 500 : g/l of TNT at saturation capacity.
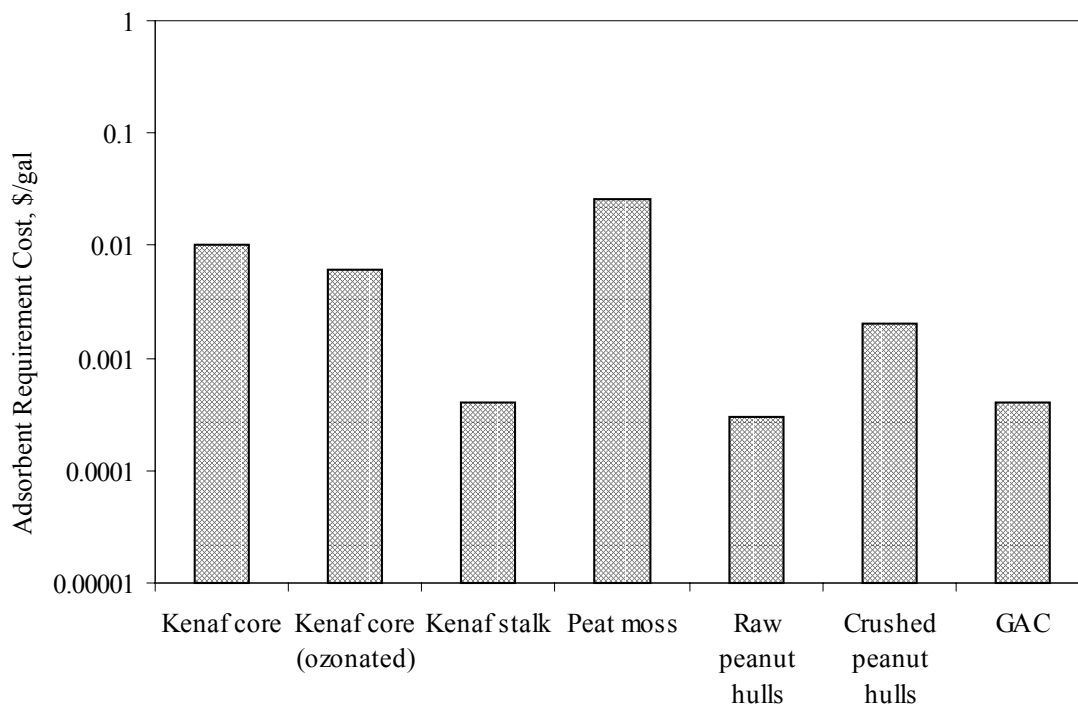
Figure 12.2. Comparison of adsorbent requirement costs for treating 5 mg/l of 2,4-DCP at saturation capacity.

Table 12.3. Adsorbent bed volume requirement per day to treat an influent containing 500 μg/l TNT at a flow rate of 100 gpm.

| Adsorbent | Adsorbent Requirement, lb | Bulk Density, lb/ft$^3$ | Bed Volume, ft$^3$ |
|---|---|---|---|
| Kenaf core | 11389 | 9 | 1265 |
| Kenaf core (ozonated) | 4953 | 9 | 550 |
| Kenaf stalk | 4384 | 6 | 730 |
| Peat moss | 4189 | 15 | 279 |
| Raw peanut hulls | 37358 | 12 | 3113 |
| Crushed peanut hulls | 2062 | 16 | 128 |
| GAC | 8 | 30 [a] | 0.277 |

Table 12.4. Adsorbent bed volume requirement per day to treat an influent containing 5 mg/l 2,4-DCP at a flow rate of 100 gpm.

| Adsorbent | Adsorbent Requirement, lb | Bulk Density, lb/ft$^3$ | Bed Volume, ft$^3$ |
|---|---|---|---|
| Kenaf core | 12762 | 9 | 1418 |
| Kenaf core (ozonated) | 6480 | 9 | 720 |
| Kenaf stalk | 11898 | 6 | 1983 |
| Peat moss | 10343 | 15 | 689 |
| Raw peanut hulls | 7586 | 12 | 632 |
| Crushed peanut hulls | 43261 | 16 | 2703 |
| GAC | 30 | 30 [a] | 1 |

a: Cooney (1999).

# CHAPTER XIII

## ENGINEERING SIGNIFICANCE

The study performed in this research can be used as a tool to determine the feasibility of using natural adsorbents such as kenaf, peat moss, and peanut hulls to treat waters contaminated with 2,4-DCP and TNT. Due to lower adsorption capacities, the adsorbent requirements for the candidate adsorbents will be higher when compared to GAC. This will lead to larger adsorbent bed volumes required for treatment when the candidate adsorbents are used. To accommodate large volumes of adsorbent to treat an influent with the candidate adsorbents, larger contactors will be required. Since there is a possibility of densifying the candidate adsorbents, the calculated bed volumes during design can be considerably reduced during actual contactor operation.

The faster breakthrough curves associated with the candidate adsorbents during continuous column studies mean that the adsorbent gets spent very fast. This will lead to the exhaustion of the adsorbent bed quickly and will require the addition of fresh or virgin adsorbent at a faster rate when compared to GAC operation. The long term benefits such as the low adsorbent cost requirements and the possibility of composting the spent adsorbent should also be considered during contactor operation.

The calculated adsorbent requirements and bed volumes are based on assuming a given influent concentration and flow rate. The actual adsorbent requirement would be

based on actual plant conditions. Though the calculated adsorption capacities give an

estimate of the adsorbent requirement and cost, the actual adsorption capacity will vary

according to the plant conditions. The Freundlich parameters were determined from

experiments conducted at room temperature and at a pH of about 5.0. Also, the

experiments were conducted for single solute systems and competitive adsorption was

not considered. Although the engineering applications would normally be carried out

under room temperature, the pH of the influent stream may vary. If the pH of the influent

stream is higher than the pKa value of the adsorbate, there is a strong possibility that

lesser adsorption would take place due to dissociation of the adsorbate molecules. It

should be noted that pH studies were not carried out with the test adsorbates on the

candidate adsorbents and suggestions are based on literature review (Chapter VI). The

influent stream may also contain a variety of organics, which may all be involved in

competing for the active sites on the adsorbent surface. This may reduce the ability of

the adsorbent to remove a particular organic compound. Also, the adsorbent

requirements are a function of the influent and effluent concentration required. Thus, it is

recommended that pilot scale experiments using the same operating conditions be carried

out with the same wastewater stream prior to design scale up.

CHAPTER XIV

CONCLUSIONS

In this research, the ability of natural adsorbents such as kenaf, peat moss, hay, and peanut hulls were studied.  In this study, adsorption isotherm data were generated for TNT and 2,4-DCP adsorption onto the natural adsorbents.  A wide concentration range of the adsorbates were used to determine the Freundlich constants (k and 1/n).  Surface oxidation techniques such as ozonation, peroxone, and combination of ultrasound and ozone were tried and their effect on the adsorption of TNT and 2,4-DCP studied. Continuous flow studies were performed to compare the adsorption capacity in continuous column operation with the capacity obtained from batch studies.

The specific conclusions made from this research are as follows :

● The equilibrium time of all the candidate adsorbents in adsorbing TNT and 2,4-DCP lies within 180 minutes.

● More than 80 % of the ultimate adsorption occurs within the first 30 minutes, after which there is a slow approach to equilibrium.

● All the candidate adsorbents except hay possess the ability to adsorb TNT and 2,4-DCP.

● Crushed peanut hulls  have the highest adsorption capacity among the candidate adsorbents for TNT adsorption.

- Raw peanut hulls have the highest adsorption capacity among the candidate adsorbents for 2,4-DCP adsorption.

- The adsorption capacities of the candidate adsorbents are significantly lower than the capacity of granular activated carbon for both TNT and 2,4-DCP adsorption.

- Surface oxidation techniques have an effect on adsorption. Increase or decrease in adsorption capacity after surface oxidation depends on the type of adsorbent, adsorbate, and equilibrium concentration. Kenaf core demonstrated an enhancement in adsorption capacity after surface oxidation for both TNT and 2,4-DCP adsorption.

- The adsorption capacity of kenaf core and raw peanut hulls during continuous column operation is comparable to the batch adsorption capacity. The adsorption capacity of kenaf stalk during continuous column operation is slightly lower than the batch adsorption capacity.

- The calculated adsorbent costs for kenaf stalk are lower than GAC for both TNT and 2,4-DCP adsorption. The calculated adsorbent costs for crushed peanut hulls are lower than GAC for TNT adsorption. The calculated adsorbent costs for raw peanut hulls are lower than GAC for 2,4-DCP adsorption. The calculated adsorbent costs for kenaf core and peat moss are higher than GAC for both TNT and 2,4-DCP adsorption.

- Much larger bed volumes are required when using the candidate adsorbents in continuous column operations due to higher adsorbent requirement when compared to GAC.

# REFERENCES

Abu-El-Shar, W.Y., Gharaibeh, S.H., and Mahmoud, S.(1999). Removal of Dyes from Aqueous Solutions Using Low-Cost Sorbents Made of Solid Residues from Olive-mill Wastes (JEFT) and Solid Residues from Refined Jordanian Oil Shale. *Environmental Geology*, 39 (10), 1090- 1094.

Acar, Y. and Zappi, M., (1995). Infrastructural Needs in Waste Containment and Environmental Restoration. *Journal of Infrastructure*, 1 (2).

Agency for Toxic Substances and Disease Registry (1992). Toxicological Profile for 2,4-Dichlorophenol. Atlanta, Georgia: US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, *DHHS (ATSDR) publication*. No. TP-91/14

Allen, S.J., Brown, P., McKay, G., and Flynn, O. (1992). An Evaluation of Single Resistance Transfer Models in the Sorption of Metal Ions by Peat. *Journal of Chemical Technology and Biotechology*, 54, 271-276.

Allen, S.J., McKay, G., and Khader, K.Y.H. (1988). Multi-Component Sorption Isotherms of Basic Dyes on Peat. Environmental Pollution, 52, 1, 39-53.

Allen, S.J., and McKay, G. (1987). Diffusion Model for the Sorption of Dyes on Peat. Journal of Separation Process Technology, 8, 18-25.

Barnett, R.L. and Clarke, O.M., Jr., (1983). Peat Resource Estimate in Alabama. Geological Survey of Alabama, Open File Report.

Benkhedda, J., Jaubert, J.N., and Barth, D. (2000). Experimental and Modeled Results Describing the Adsorption of Toluene onto Activated Carbon. *Journal of Chemical Engineering Data*, 45,650-653.

Belkevich, P.I., Gayduk, K.A., and Christova, L.R. (1976). Role of Peat in Decontamination of Environment. Proceedings of 5th International Peat Congress, 1, 328-348.

Boardsell, D.V., Nichols D.G., and Jones D.L., (1979). Physical Properties of Nursery Potting- Mixtures, *Scientia Horticulturae* 11, 1-8.

Brunauer, S., Emmett, P.H., and Teller, E.(1938). Adsorption of Gases in Multimolecular Layers. *Journal of American.Chemical Society*,60 (309),1938.

Brown, P., Jefcoat I.A., Parrish D., Gill S., Graham, E., (2000). Evaluation of the Adsorptive Capacity of Peanut Hulls Pellets for Heavy Metal in Solution. *Advances in Environmental Research* 4, 19-29.

Calgon Carbon Corporation.  http://www.calgoncarbon.com

Cardoso, J.B., and Clarke, O.M.(1985). Use of Alabama Peat as an Adsorbent for Heavy Metals. Mineral Resources Institute, School of Mines and Energy Development.

Caturla, F., Martin-Martinez, J.M., Molina-Sabio, M., Rodriguez-Reinoso, F., Torregrosa,  R.(1988). Adsorption of Substituted Phenols on Activated Carbon. *Journal of Colloid and  Interface Science*, 124(2), 528-534.

Chaney, R.L., and Hundermann, P.T.(1979).Use of Peat Moss Columns to Remove Metal Ions from Wastewater. *Journal of Water Pollution Control Federation*, 51, 17-21.

Chungtai, F.A., Fakhar-un-Nisa, Illahi, A., Ejaz-ul-Haque, and Parveen N.(1987). Activated Carbon from a Tropical Carbonaceous Material. *Journal of Pure and Applied Sciences*, 6(1), 57-60.

Clark, S., Brown, P., and Pitt, R. (1999).Wastewater Treatment Using Low-  Cost Adsorbents and Waste Materials. Department of Civil and Environmental Engineering, University of Alabama at Birmingham, University of Alabama at Tuscaloosa, Alabama.

Colella, L.S., Armenante, P.M., (1998). Adsorption Isotherms for Chlorinated Phenols on Activated Carbon. *Journal of Chemical Engineering Data*, 43, 573-579.

Construction Engineering Research Laboratory (CECER). Treatment of Wastewater from Munitions  Production. http://www.cecer.army.mil/td/tips/product/details.cfm?ID=572.

Cooney, David O., (1999). Adsorption Design for Wastewater Treatment. Lewis Publishers, CRC  Press LLC, Boca Raton, Florida.

Corapcioglu, M.O. and Huang, C.P. (1987). The Surface Acidity and Characterization of Some Commercial Activated Carbons. *Carbon*, 25, 569.

Coughlin, R.W.; Ezra, F.S. (1968). *Environmental Science Technology*,2(4), 291.

Crittende, B., and Thomas, W.J. (1998). Adsorption Technology and Design. Butterworth- Heinemann Publishers.

Davis, S.W., Powers, S.E. (2000).  Alternative Sorbents for Removing MTBE from Gasoline-Contaminated Ground Water.  Journal of Environmental Engineering, 126 (4), 345-360.

Daun, G., Lenke, H., Reuss, M., and Knackmuss, H.J.(1998). Bilological Treatment of TNT-Contaminated soil. 1.Anaerobic Cometabolic Reduction and Interaction of TNT and Metabolites with Soil Components. *Environmental Science and Technology*, 32, 1956-1963

Dobbs, R.A., and Cohen, J.M. (1980). Carbon Adsorption Isotherms for Toxic Organics. Municipal Environmental Research Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio.

Dueitt,S.,D. (1994). Rice Hulls as a Substitute for Sphagnum Peat Moss in a Sphagnum Peat Based Green House Media, MS Thesis, Department of Plant and Soil Sciences, Mississippi State University.

Eichenmuller, B., Bunke, G., Behrend, K., Buchholz, R., and Gotz, P.(1997). Adsorption of Acenaphthene on Porous Organic Polymers. *Journal of Environmental Engineering*, 123 (9), 836-841.

Farrier,D.D.;Hines,A.L.;Wang, S.W. (1979). Adsorption of Phenol and Benzoic acid from Dilute Solutions onto a Macrorecticular Resin. *Journal of Colloid and Interface Science*,69,233-237.

Fleming, E., Bricka, R., and Bailey, S. (1995). Ultraviolet/Chemical Oxidation Treatment of RDX-Contaminated Waters at Picatinny Arsenal. Report No.EL-95-7, USAE Waterways Experiment Station, Vicksburg, Mississippi.

Freistad, H.O., Ott, D.E., and Gunther, F.A.(1969). Automated Colorimetric Micro determination of Phenols by Oxidative Coupling with 3-Methyl-2-Benzothiazoline Hydrazone. *Analytical Chemistry*, 41,1750.

Gonzalez, l.,  J.de D., Valenzuela-Calahorro, C., Navarette-Guijosa, A., and Gomez-Serrano, V. (1998). Adsorption of p-nitrophenol by Active Carbons Prepared from Olive Wood. *Ann.Quim.Ser.B*., 84(1),47-51.

Gowan, J.L. (1997). <u>An Economic Analysis of Alternative Harvesting Techniques for Kenaf</u>. MS Thesis in Agricultural Economics, Department of Agricultural Economics, Mississippi State University.

Gupta, G.S., Prasad, G., and Singh, V.N. (1990).<u>Removal of Chrome Dye from Aqueous Solutions by Mixed Adsorbents Fly Ash and Coal</u>. *Water Resource*, 24(11), 45-50.

Gupta, V..K. (1998). <u>Equlibrium Uptake, Sorption Dynamics, Process Development, and Column Operations for the Removal of Copper and Nickel from Aqueous Solution and Wastewater Using Activated Slag, a Low-Cost Adsorbent.</u> *Industrial and Engineering Chemistry Research*,37,192- 202.

Haas, C. and Vamos,R., (1995). <u>Hazardous and Industrial Waste Treatment</u>. Prentice-Hall Inc., New York, New York.

Han, J.S.(1999). <u>Stormwater Filtration of Toxic Heavy Metal Ions Using Lignocellulosic Materials Selection Process, Fiberization, Chemical Modification, and Mat Formation</u>. U.S.Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisconsin, U.S.A.

Handerlein, S.B., and Schwarzenbach, R.P.(1993). <u>Adsorption of Substituted Nitrobenzenes and Nitrophenols to Mineral Surfaces</u>. *Environmental.Science and Technology*, 27, 316-326.

Haas, R., Von Low, E. (1986). Forum Städte-Hyg. 37, 33-43.

Hassler,J.W., (1963). <u>Activated Carbon</u>. Chemical Publishing Co., New York.

Henderson, R.W., Andrews, D.S., Lightsey, G.P., Poonawala, N.A.(1977). <u>Reduction of Mercury, Copper, Nickel, Cadmium, and Zinc Levels in Solution by Competitive Adsorption onto Peanut Hulls, and Raw and Aged Bark</u>. *Bulletin of Environmental Contamanitation and Toxicology*, 17 (3), 355-359.

Hindarso, H., Ismadji, S., Wicaksana, F., Mudjijati, and Indraswati, N.(2001). <u>Adsorption of Benzene and Toluene from Aqueous Solution onto GranularActivated Carbon</u>. *Journal of Chemical Engineering Data*, 46, 788-791.

Ho,P. and Daw, C.(1988). *Environmental  Science and Technology,* 22(8), 919-924.

Howard, P.H. (1993). <u>Handbook of Environmental Fate and Exposure Data for Organic Chemicals</u>. Volume IV-Solvents 2, Lewis Publishers, Boca Raton, Florida.

Hughes, J.B., Shanks, J., Vanferford, M., Lauritzen, J., and Bhadra, R. (1997). Transformation of TNT by Aquatic Plants and Plant Tissue Cultures. *Environmental Science and Technology*, 31,266-271

Gomaz, M.J., Garcia, G.A., Martinez, S.C., and Solano, L.A.(1996). Activated Carbon from Spanish Coal, Chemical Activation. *Energy & Fules*, 10,1108-1114.

Ishizaki, C., and Marti, I. (1981). Surface Oxide Structures on a Commercial Activated Carbon. *Carbon*, 19, 409.

Itaya,A., Kato, N.,Yamamoto (1978). Liquid Phase Adsorption Equilibrium of Phenol and its Derivatives on Macro Reticular Adsorbents. *Journal of Chemical Engineering Science*, 33,1097-1106.

Jossens,L., Prausnitz, J.M., Fritz, W., Schlunder, E.U., Myers, A.L.(1978). Thermodynamics of Mulit-Solutes Adsorption from Dilute Aqueous Solutions. *Chemical Engineering Science*, 17, 389-395.

Juang,R.S., Feng-Chin Wu, Ru-Ling Tseng (1996). Adsorption Isotherms of Phenolic Compounds from Aqueous Solutions onto Activated Carbon Fibers. *Journal of Chemical Engineering Data*, 41, 487-492.

Kim, J.MY., Jae K.Park, and Tuncer B.Edil.(1997). Sorption of Organic Compounds in the Aqueous Phase onto Tire Rubber. *Journal of Environmental Engineering*, 123(9), 827-835.

Kogya, K.K., and Kaisha, K.(1988). Method and Apparatus for Activating Infusibilized Pitch Beads. European Patent 317 217.

Kugler, Daniel E., (1988). Kenaf Newsprint: Realizing Commercialization of a New Crop after Four Decades of Research and Development. USDA CSRS Report on the kenaf demonstration project, Washington D.C.

Kumar, S., Upadhyay, S.N., and Upadhya, Y.D.(1987). Removal of Phenols by Adsorption on Fly Ash. *Journal of Chemical Technoloy and Biotechnology*, 37, 281-290

LaGrega, M., Buckingham, P., Evans, J., and the Environmental Resources Management Group, (1994). Hazardous Waste Management. McGraw-Hill Inc., New York, NY.

Langlais, b., Reckhow, D., and Brink, D., (1991). Ozone in Water Treatment. Lewis Publishers, Chelsea, Michigan.

Langmuir, K.(1918). *Journal of Chemical Society*, 40,1361

Larry, W.M.(1983) Utilization of Selected Agricultural Residues for Heavy Metal Removal, Dissertation submitted to the faculty of the department of civil engineering, Mississippi State University.

Lee, J., Henke, M.S.E. and Speitel, G.E. (1998). Performance Evaluation of Granular Activated Carbon System at Pantex: Rapid Small-Scale Column Tests to Simulate Removal of High Explosives from Contaminated Groundwater. NRCP-1998-10.

Lennard-Jones, J.E. and Dent, B.M. (1928) *Transactions of the Faraday Society*, 24, 92

Lennard-Jones,J.E.(1932).*Transactions of the Faraday Society*, 28, 333.

Leslie, M.E. (1974). Peat. New Medium for Treating Dye House Effluent. Am.Dyest.Rep.,63, 8, 15-18.

London, F., Theory and Systematics of Molecular Forces, *Z.Phys*., 63, 245, 1930

Lucchesi, A. and Maschio, G.(1983). Semi-Active Carbon and Aromatics Produced from the Pyrolysis of Scrap Tyres. *Conserv. Recyc*., 6(3), 85-90.

Magne, P., Walker ,P.L. Jr. (1986). *Carbon*, 24(2), 101.
McBain, J.W.(1935). *Journal of American Chemical Society*, 57, 699

McKay, (1996). Use of Adsorbents for the Removal of Pollutants from Wastewaters. CRC  Press.

Metcalf and Eddy (1991). Wastewater Engineering. McGraw-Hill, NY.

Mueller, W.F., Bedell, G.W., Jackson, P.J.(1993). Biodegradation of Explosives. Technical completion report, Project number: WERC-89-059. New Mexico waste-management education and research consortium.

Nagendra Rao, C.R., Iyengar, L., and Venkabachor, C.(1993). Sorption of copper(II) from Aqueous Phase by Waste Biomass. *Journal of Environmental.Engineering* Division, ASCE, 119(2), 369-377

National Agricultural Statistics Service, (1997). http://www.usda.gov/nass

Nawar, S.S. and Doma, H.S.(1989). Removal of Dyes from Effluents Using Low-Cost Agricultural by-products. *Science of the Total Environment*, 79, 271-279.

Norit Activated Carbon.  http://www.norit.com

Okieimen, F.E., Okundia, E.U., Ogbeifun, D.E. (1991). Sorption of Cadmium and Lead Ions on Modified Groundnut (*Arachis hypogea*) Husks. *Journal of Chemical Technology and Biotechnology*. 51, 97-103.

Paprowicz, J.T.(1990). Activated Carbons for Phenols Removal from Wastewaters. *Environmental Technology*, 11, 71-82.

Periyasamy, K., and Namasivayam,C., (1994). Process Development for Removal and Recovery of Cadmium from Waste-water by a Low Cost Adsorbent: Adsorbent Rates and  Equilibrium Studies. *Industrial and Engineering Chemistry Research*, 33(2), 317-320.

Pollard, S.J.T., Fowler,G.D., Sollars,C.J., and Perry, R.(1992). Low-cost Adsorbents for Wastewater Treatment: A Review. *The Science of the Total Environment*, 116, 31-52.

Preuss, J., Haas, R.(1988). G.Geogr.Rundschau, 40 (6), 31-38.

Puri, B.R. (1983). Physicochemical Aspects of Carbon Affecting Adsorption from the Aqueous Phase, Treatment of Water by Granular Activated Carbon.  *Advances in Chemistry Series*, 202,American Chemical Society.

Puri, B.R.; Kaistha, B.C.; Mahajan, O.P. (1966). *Journal of Indian Chemical Society*, 1963, 4880-4.

Puri, B.R.; Mahajan, O.P.Gandhi, D.L. (1972). *Journal of Indian Chemical Society*,10,848-9.

Radke,C.J. and Prausnitz,J.M., (1972). Adsorption of Organic Solutes from Dilute Aqueous Solution on Activated Carbon. *Industrial Engineering and Chemistry Research*, 11, 445.

Redlich,O.;Peterson,D.L.(1959).A Useful Adsorption Isotherm. *Journal of Physical Chemistry*, 63, 1024.

Schulte, G., Hoehn, R. and Randall, C. (1973). The Treatability of Munitions-Manufacturing Waste with Activated Carbon. Proceedings of the 28th Industrial Waste Conference, May 1-3, Purdue University, Lafayette, Ind.

Seidel, A., Tzscheutschler, E., Radke, K.H., and Gelbin, D.(1985). <u>Adsorption Equilibria of Aqueous Phenol and Indol Solutions on Activated Carbons</u>. *Chemical Engineering Science*, 40 (2), 215-222.

Smith, J.A., Novak, J.T.(1987). <u>Biodegradation of Chlorinated Phenols in Surface Soils</u>. *Water, Air, Soil Pollution*, 33, 29-42.

Snoeyink, V.L., McCreary, J.J., Murin, C.J.(1977). <u>Carbon Adsorption of Trace Organic Compounds</u>. Municipal Research Lab, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Speitel, G.E. (1999). <u>Treatment of High Explosives by Adsorption and Biodegradation on GAC.</u> Proposal, The University of Texas at Austin. http://www.pu.org/main/plans/ plenv99.html#headsorp.

Srinivasan,K., Rao, P.B.S., and Ramadevi, A.(1988). <u>Studies on Characteristic of Carbon Obtained from Tamarind Nuts</u>. *Indian Journal of Environmental Health*, 30(1), 303-305.

Srivastava, S.K., Tyagi, R., and Pal, N.(1989).<u>Studies on the Removal of Some Toxic Metal Ions.Part II: Removal of Lead and Cadmium by Montmorillonite and Kaolinite</u>. *Environmental Technology Letters*, 10,275-282.

Srivastava, S.K., Singh, A.K., and Sharma, A.(1994). <u>Studies on the Uptake of Lead and Zinc by Lignin Obtained from Black Liquor-A Paper Industry Waste Material</u>. *Environmental Technology*, 15, 353-361.

Srivastava, S.K., Tyagi, R., and Pant, N.(1989). <u>Adsorption of Heavy Metal Ions on Carbonaceous Material Developed from the Waste Slurry Generated in Local Fertilizer Plants</u>. *Water Res*., 23(9), 1161-1165.

Srivastava, S.K., Tyagi, R., Pal, N., Mohan, D.(1997). <u>Process Development for Removal of Substituted Phenol by Carbonaceous Adsorbent Obtained from Fertilizer Waste</u>. *Journal of Environmental Engineering*, 123 (9), 842-851.

Stoeckli, F., Ramon, M.V.L., and Castilla, C.M.(2001). <u>Adsorption of Phenolic Compounds from Aqueous Solutions by Activated Carbons, Described by the Dubinin-Astakhov Equation</u>. *Langmuir*, 17, 3301-3306.

Suttie, J.,M. (2000). Hay and Straw Conservation for Small-Scale Farming and Pastoral Conditions. <u>Food and Agriculture Organization of the United Nation</u>, Rome.

Tanin, S. and Gurgey, I.(1988). <u>Bleaching of Cottonseed and Sunflower Oils by Active</u>

Carbons from Rice Hulls. Chim. Acta Turica, 16, 209-219.

Tessmer, C.H., Vidic, R.D., and Uranowski, L.J. (1997). Impact of Oxygen-Containing Surface Functional Groups on Activated Carbon Adsorption of Phenols. *Environmental Science Technology*, 31,1872-1878.

U.S. Geological Survey, Industrial Use (1995). http://ga.water.usgs.gov/edu/wuin.html

US Army Corps of Engineers (2000). Engineering Research and Development Center. Construction Engineering Research Laboratory, Champaign. Illinois 61826-9005.

U.S.Army Toxic and Hazardous Materials Agency Report No.CETHA-TE-CR-90041, OSHA, Aberdeen Proving Ground, Md.

United States Army Environmental Center (2000). http://aec.army.mil/prod/usaec/et/comp/pinkwater.htm

United States Environmental Protection Agency (1997). http://www.epa.gov/oppt/24dcp.htm.

United States Environmental Protection Agency (1973). Process Design Manual for Carbon Adsorption. USEPA Technology transfer.

United States Environmental Protection Agency (1975). Preliminary Assessment of Suspected Carcinogens in Drinking Water. Interior Report to Congress, Office of Toxic Substances, Washington, D.C.

United States Environmental Protection Agency (1980). Ambient Water Quality Criteria for 2,4-Dichlorophenol. EPA 440/5-80-042. Office of water regulations and standards criteria and standards division, Washington DC.

USATHAMA Report (1987). Granular Activated Carbon (GAC) System Performance Capabilities and Optimization.

Vazquez, G., Antorrena, G., Gonzalez, J., Doval, M.D. (1994). Adsorption of Heavy Metal Ions by Chemically Modified Pinus Pinaster Bark. Elsevier Science limited, 0960-8524/94.

Vidic, R.D., Suidan, M.T., Brenner, R.C. (1993). *Environmental Science and Technology*, 27(10), 2079

Waiss Jr., A.C., Wiley, M.E., Kuhnle, J.A., Potter, A.L., McCready, R.M.(1973). Adsorption of Mercuric Cations by Tannins in Agricultural Residues. *Journal of*

*Environmental Quality*, 2, 369-371.

Ward, T.M. and Getzen, F.W., (1970). Influence of Ph on the Adsorption of Aromatic Acids on Activated Carbon. *Environmental Science and Technology*, 4, 64.

Whong, W.Z., Edwards, G.S.(1984). *Mutation Res.*, 136, 209-215.

Whightman, J.P., Dole, L.R., Jones, King, C.A.(1971). Adsorption of Organic Compounds onto Solids from Aqueous Solutions. Water Resources Research Center, Virginia Polytechnic Institute and State University, Blackburg, Virginia, Bulletin 42.

Wujcik, W.J., Lowe, W.L., Marks, P.J., and Sisk, W.E. (1992). Granular Activated Carbon Pilot Treatment Studies for Explosive Removal From Contaminated Groundwater. *Environmental Progress*, 11 (3), 178-189.

Wujcik, W., Lowe, W., and Marks, P. (1990). Use of Activated Carbon for Treatment of Explosives Contaminated Groundwater at the Milan Army Ammunition Plant (MAAP).

Zappi, M., Gunnison, D., Pennington, J., Cullinane, M., Brannon, J., and Myers, T., (1993). Technical Approach for Insitu Biological Treatment Research: Bench-Scale Experiments. Report No. IRRP-93-3, USAE Waterways Experiment Station, Vicksburg, Mississippi.

Zappi, M., (1995). Peroxone Oxidation Treatment of 2,4,6-Trinitrotoluene Contaminated Waters With and Without Sonolytic Catalyzation. Dissertation submitted to the Faculty of the Department of Chemical Engineering, Mississippi State University

Zappi, M.E.(1998). Groundwater Treatment of Explosives Contamination. Encyclopedia of Environmental Analysis and Remediation, John Wiley & Sons, Inc.

Zappi, M., Graves, K.,Aycock, A.,Subramani, A.,Tavai, S., Development of kenaf-based biosorptive water treatment process. Technical Interim Report, Project Number 1434-HQ-96-GR-O2679-20, Water Resources Research Institute, Mississippi State University, April 2000.

Zogorski, J.S., Faust, S.D., Haas, J.H. Jr., (1976). The Kinetics of Adsorption of Phenols by Granular Activated Carbon. *Journal of Colloid and Interface Science*, 55 (2).

APPENDIX A

INITIAL BATCH STUDIES DATA

Table A.1. Single component equilibrium time experimental data for kenaf core using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
| --- | --- |
| 0 | 16.44 |
| 30 | 9.69 |
| 60 | 9.53 |
| 120 | 9.45 |
| 210 | 9.35 |
| 270 | 9.32 |

Table A.2. Single component equilibrium time experiments data for kenaf core using TNT.

| Time, minutes | Residual Concentration, mg/l |
| --- | --- |
| 0 | 3.7 |
| 30 | 2.21 |
| 60 | 2.22 |
| 90 | 2.01 |
| 120 | 2.02 |
| 150 | 1.87 |
| 180 | 1.95 |
| 240 | 2.02 |

Table A.3. Single component equilibrium time experiments data for kenaf stalk using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
| --- | --- |
| 0 | 16.25 |
| 30 | 11.78 |
| 60 | 12.66 |
| 120 | 11.00 |
| 210 | 9.78 |

Note: All residual concentrations shown are average values of two samples (individual sample concentrations were not significantly different).

Table A.4. Single component equilibrium time experiments data for kenaf stalk using TNT.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 14.85 |
| 30 | 10.20 |
| 60 | 10.24 |
| 90 | 9.97 |
| 120 | 9.79 |
| 180 | 9.99 |

Table A.5. Single component equilibrium time experiments data for peat moss using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 19.22 |
| 30 | 9.81 |
| 60 | 9.31 |
| 120 | 8.66 |
| 210 | 8.55 |

Table A.6. Single component equilibrium time experiments data for peat moss using TNT.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 3.95 |
| 30 | 1.79 |
| 60 | 1.55 |
| 90 | 1.15 |
| 120 | 1.23 |
| 180 | 1.26 |

Table A.7. Single component equilibrium time experiments data for raw peanut hulls using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 14.50 |
| 30 | 8.10 |
| 120 | 6.50 |
| 180 | 5.65 |
| 240 | 6.381 |
| 300 | 5.36 |

Table A.8. Single component equilibrium time experiments data for raw peanut hulls using TNT.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 18.84 |
| 30 | 13.01 |
| 120 | 15.01 |
| 180 | 14.00 |
| 240 | 14.51 |
| 300 | 13.92 |

Table A.9. Single component equilibrium time experiments data for crushed peanut hulls using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 14.50 |
| 30 | 10.06 |
| 120 | 8.39 |
| 180 | 6.70 |
| 300 | 6.10 |

Table A.10. Single component equilibrium time experiments data for crushed peanut hulls using TNT.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 39.36 |
| 30 | 29.21 |
| 60 | 27.11 |
| 120 | 26.94 |
| 180 | 26.04 |
| 240 | 25.13 |
| 300 | 24.16 |
| 360 | 24.29 |

Table A.11. Single component equilibrium time experiments data for hay using 2,4-DCP.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 19.72 |
| 30 | 15.77 |
| 60 | 17.15 |
| 120 | 17.23 |
| 210 | 17.03 |
| 270 | 16.89 |

Table A.12. Single component equilibrium time experiments data for hay using TNT.

| Time, minutes | Residual Concentration, mg/l |
|---|---|
| 0 | 40.82 |
| 30 | 29.96 |
| 75 | 29.44 |
| 150 | 25.70 |
| 210 | 25.55 |
| 270 | 26.14 |

APPENDIX B

ADSORPTION ISOTHERMS DATA

Table B.1. Adsorption isotherm data for TNT on kenaf core.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 2.024 | 0.012 | 0.243 |
| 0.1 | 1.902 | 0.015 | 0.158 |
| 0.15 | 1.755 | 0.020 | 0.134 |
| 0.2 | 1.571 | 0.025 | 0.128 |
| 0.25 | 1.478 | 0.028 | 0.114 |
| Blank | 2.410 | | |

Initial TNT concentration (Co) = 2.43 mg/l          Volume (V) = 0.04 l

X = (Co - Cf) x V


Table B.2. Adsorption isotherm data for TNT on kenaf core.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 12.563 | 0.156 | 3.121 |
| 0.1 | 9.093 | 0.260 | 2.601 |
| 0.15 | 8.850 | 0.267 | 1.783 |
| 0.25 | 8.246 | 0.285 | 1.142 |
| 0.35 | 6.137 | 0.348 | 0.996 |
| Blank | 17.245 | | |

Initial TNT concentration (Co) = 17. 766 mg/l          Volume (V) = 0.04 l


Note :

X = (Co - Cf) x V

All residual concentrations (Cf) shown are average values of two samples (individual sample concentrations were not significantly different).

Blank served as the control.

Table B.3. Adsorption isotherm data for TNT on kenaf stalk.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.05 | 1.018 | 0.019 | 0.397 |
| 0.1 | 0.930 | 0.023 | 0.233 |
| 0.15 | 0.953 | 0.022 | 0.149 |
| 0.2 | 0.847 | 0.026 | 0.133 |
| Blank | 1.497 | | |

Initial TNT concentration (Co) = 1.515 mg/l        Volume (V) = 0.04 l

Table B.4. Adsorption isotherm data for TNT on kenaf stalk.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 12.080 | 0.187 | 3.750 |
| 0.15 | 10.347 | 0.239 | 1.596 |
| 0.25 | 7.682 | 0.319 | 1.277 |
| 0.35 | 6.109 | 0.366 | 1.047 |
| 0.45 | 3.846 | 0.434 | 0.965 |
| Blank | 18.150 | | |

Initial TNT concentration (Co) = 18.33 mg/l        Volume (V) = 0.03 l

Table B.5. Adsorption isotherm data for TNT on kenaf stalk.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 27.576 | 0.542 | 3.615 |
| 0.25 | 25.478 | 0.626 | 2.505 |
| 0.35 | 22.333 | 0.752 | 2.148 |
| 0.45 | 19.197 | 0.877 | 1.949 |
| 0.55 | 17.237 | 0.955 | 1.738 |
| 0.65 | 13.231 | 1.116 | 1.717 |
| Blank | 40.119 | | |

Initial TNT concentration (Co) = 41.135 mg/l          Volume (V) = 0.04 l

Table B.6. Adsorption isotherm data for TNT on peat moss.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 1.769 | 0.020 | 0.402 |
| 0.1 | 1.438 | 0.030 | 0.300 |
| 0.15 | 1.150 | 0.038 | 0.257 |
| 0.2 | 1.012 | 0.0428 | 0.214 |
| 0.25 | 0.880 | 0.046 | 0.187 |
| Blank | 2.392 | | |

Initial TNT concentration (Co) = 2.44 mg/l          Volume (V) = 0.03 l

Table B.7. Adsorption isotherm data for TNT on peat moss.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 14.004 | 0.096 | 1.929 |
| 0.1 | 13.706 | 0.108 | 1.084 |
| 0.2 | 10.301 | 0.244 | 1.223 |
| 0.3 | 8.704 | 0.308 | 1.028 |
| 0.4 | 7.781 | 0.345 | 0.863 |
| Blank | 16.404 | | |

Initial TNT concentration (Co) = 16.417 mg/l          Volume (V) = 0.04 l

Table B.8. Adsorption isotherm data for TNT on peat moss.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 36.810 | 0.124 | 2.480 |
| 0.1 | 34.163 | 0.229 | 2.298 |
| 0.2 | 29.096 | 0.432 | 2.162 |
| 0.3 | 24.295 | 0.624 | 2.082 |
| 0.4 | 21.870 | 0.721 | 1.804 |
| Blank | 39.910 | | |

Initial TNT concentration (Co) = 39.964 mg/l          Volume (V) = 0.04 l

Table B.9. Adsorption isotherm data for TNT on peat moss.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.15 | 54.407 | 0.530 | 3.534 |
| 0.25 | 48.458 | 0.768 | 3.072 |
| 0.35 | 41.435 | 1.049 | 2.997 |
| 0.45 | 36.017 | 1.265 | 2.812 |
| 0.55 | 28.714 | 1.557 | 2.832 |
| 0.65 | 28.914 | 1.549 | 2.384 |
| 0.75 | 27.873 | 1.591 | 2.122 |
| Blank | 67.620 | | |

Initial TNT concentration (Co) = 67.661 mg/l          Volume (V) = 0.04 l

Table B.10. Adsorption isotherm data for TNT on raw peanut hulls.

| Mass of Raw Peanut Hulls, gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed, mg | X/M , mg/gm |
|---|---|---|---|
| 0.25 | 15.445 | 0.092 | 0.371 |
| 0.35 | 14.708 | 0.122 | 0.349 |
| 0.45 | 13.984 | 0.151 | 0.336 |
| 0.55 | 13.423 | 0.173 | 0.315 |
| Blank | 17.617 | | |

Initial TNT concentration (Co) = 17.766 mg/l          Volume (V) = 0.04 l

Table B.11. Adsorption isotherm data for TNT on raw peanut hulls.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.25 | 34.019 | 0.204 | 0.818 |
| 0.45 | 31.101 | 0.321 | 0.713 |
| 0.65 | 28.779 | 0.414 | 0.637 |
| 0.85 | 27.803 | 0.453 | 0.533 |
| 1.05 | 24.226 | 0.596 | 0.567 |
| 1.15 | 25.086 | 0.561 | 0.488 |
| 1.35 | 22.153 | 0.679 | 0.503 |
| Blank | 38.378 | | |

Initial TNT concentration (Co) = 39.133 mg/l          Volume (V) = 0.04 l

Table B.12. Adsorption isotherm data for TNT on crushed peanut hulls.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.15 | 14.669 | 0.171 | 1.141 |
| 0.25 | 12.339 | 0.264 | 1.058 |
| 0.35 | 9.833 | 0.364 | 1.042 |
| 0.45 | 7.917 | 0.441 | 0.980 |
| Blank | 18.815 | | |

Initial TNT concentration (Co) = 18.952 mg/l          Volume (V) = 0.04 l

Table B.13. Adsorption isotherm data for TNT on crushed peanut hulls.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 33.527 | 0.275 | 1.833 |
| 0.25 | 29.851 | 0.422 | 1.688 |
| 0.35 | 27.434 | 0.518 | 1.482 |
| 0.45 | 24.628 | 0.631 | 1.402 |
| 0.55 | 20.837 | 0.782 | 1.423 |
| Blank | 38.815 | | |

Initial TNT concentration (Co) = 40.403 mg/l        Volume (V) = 0.04 l

Table B.14. Adsorption isotherm data for TNT on hay.

| Mass of Hay (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.05 | 37.147 | 0.126 | 2.527 |
| 0.2 | 30.736 | 0.382 | 1.914 |
| 0.4 | 23.481 | 0.673 | 1.682 |
| 0.5 | 20.187 | 0.804 | 1.609 |
| Blank | 40.304 | | |

Initial TNT concentration (Co) = 40.307 mg/l        Volume (V) = 0.04 l

Table B.15. Adsorption isotherm data for TNT on kenaf core.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.1 | 36.878 | 0.218 | 2.181 |
| 0.15 | 35.633 | 0.267 | 1.786 |
| 0.2 | 33.852 | 0.339 | 1.696 |
| 0.25 | 31.308 | 0.440 | 1.763 |
| 0.3 | 29.517 | 0.512 | 1.708 |
| 0.35 | 29.693 | 0.505 | 1.444 |
| 0.4 | 28.113 | 0.568 | 1.421 |
| Blank | 41.653 | | |

Initial TNT concentration (Co) = 42.333 mg/l          Volume = 0.04 l


Table B.16. Adsorption isotherm data for TNT on kenaf core after 1 hour of ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.15 | 29.724 | 0.329 | 2.199 |
| 0.25 | 27.709 | 0.410 | 1.642 |
| 0.35 | 27.074 | 0.435 | 1.245 |
| 0.45 | 22.698 | 0.611 | 1.357 |
| 0.55 | 21.390 | 0.663 | 1.2060 |
| 0.65 | 19.894 | 0.723 | 1.112 |
| Blank | 36.995 | | |

Initial TNT concentration (Co) = 37.973 mg/l          Volume (V) = 0.04 l

Table B.17. Adsorption isotherm data for TNT on kenaf core after 2 hours of ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 31.464 | 0.386 | 1.544 |
| 0.35 | 29.395 | 0.469 | 1.340 |
| 0.45 | 26.298 | 0.592 | 1.317 |
| 0.55 | 23.590 | 0.701 | 1.274 |
| 0.65 | 21.946 | 0.766 | 1.179 |
| Blank | 38.092 | | |

Initial TNT concentration (Co) = 41.120 mg/l            Volume (V) =0.04 l


Table B.18. Adsorption isotherm data for TNT on kenaf stalk after 2 hours of ozone pretreatment.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 31.024 | 0.402 | 1.608 |
| 0.35 | 28.890 | 0.487 | 1.393 |
| 0.45 | 22.921 | 0.726 | 1.614 |
| 0.55 | 22.218 | 0.754 | 1.371 |
| 0.65 | 21.854 | 0.594 | 0.914 |
| Blank | 38.980 | | |

Initial TNT concentration (Co) = 41.08 mg/l            Volume (V) = 0.04 l

Table B.19. Adsorption isotherm data for TNT on peat moss after 1 hour of ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M , mg/gm |
|---|---|---|---|
| 0.15 | 27.091 | 0.432 | 2.886 |
| 0.25 | 23.931 | 0.559 | 2.237 |
| 0.35 | 21.336 | 0.663 | 1.894 |
| 0.45 | 21.376 | 0.826 | 1.837 |
| 0.55 | 17.042 | 0.834 | 1.518 |
| 0.65 | 15.540 | 0.895 | 1.376 |
| 0.85 | 13.165 | 0.989 | 1.164 |
| 1.05 | 10.626 | 1.091 | 1.039 |
| 1.15 | 12.097 | 1.290 | 1.122 |
| Blank | 38.377 | | |

Initial TNT concentration (Co) = 37.916 mg/l          Volume (V) = 0.04 l

Table B.20. Adsorption isotherm data for TNT on peat moss after 2 hours of ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 29.124 | 0.310 | 1.242 |
| 0.35 | 26.245 | 0.425 | 1.216 |
| 0.45 | 23.341 | 0.541 | 1.204 |
| 0.55 | 20.525 | 0.654 | 1.189 |
| 0.65 | 19.180 | 0.708 | 1.089 |
| Blank | 37.934 | | |

Initial TNT concentration (Co) = 36.887 mg/l          Volume (V) = 0.04 l

Table B.21. Adsorption isotherm data for TNT on peat moss after 4 hours of ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 22.734 | 0.298 | 1.991 |
| 0.25 | 19.583 | 0.424 | 1.699 |
| 0.35 | 16.618 | 0.543 | 1.552 |
| 0.45 | 14.442 | 0.630 | 1.400 |
| 0.55 | 13.108 | 0.683 | 1.243 |
| 0.65 | 12.124 | 0.723 | 1.112 |
| 0.75 | 10.506 | 0.787 | 1.050 |
| Blank | 30.035 | | |

Initial TNT concentration (Co) = 30.202 mg/l          Volume (V) = 0.04 l

Table B.22. Adsorption isotherm data for TNT on raw peanut hulls after 2 hours of ozone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 30.674 | 0.167 | 1.115 |
| 0.35 | 27.329 | 0.301 | 0.860 |
| 0.55 | 25.833 | 0.361 | 0.656 |
| 0.75 | 24.340 | 0.420 | 0.560 |
| 0.95 | 22.251 | 0.504 | 0.530 |
| Blank | 36.672 | | |

Initial TNT concentration (Co) = 34.858 mg/l          Volume = 0.04 l

Table B.23. Adsorption isotherm data for TNT on crushed peanut hulls after 2 hours of ozone pretreatment.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 32.834 | 0.261 | 1.0479 |
| 0.35 | 30.560 | 0.352 | 1.008 |
| 0.45 | 29.903 | 0.379 | 0.842 |
| 0.55 | 27.801 | 0.463 | 0.842 |
| 0.65 | 26.623 | 0.510 | 0.785 |
| 0.85 | 23.810 | 0.622 | 0.732 |
| 1.05 | 22.153 | 0.689 | 0.656 |
| 1.15 | 20.986 | 0.735 | 0.639 |
| Blank | 38.826 | | |

Initial TNT concentration (Co) = 39.384 mg/l          Volume (V) = 0.04 l

Table B.24. Adsorption isotherm data for TNT kenaf core after peroxone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 26.356 | 0.357 | 2.380 |
| 0.25 | 24.622 | 0.426 | 1.705 |
| 0.35 | 23.155 | 0.485 | 1.386 |
| 0.45 | 20.200 | 0.603 | 1.340 |
| 0.55 | 18.423 | 0.674 | 1.226 |
| Blank | 36.634 | | |

Initial TNT concentration (Co) = 35.284 mg/l          Volume (V) = 0.04 l

Table B.25. Adsorption isotherm data for TNT kenaf stalk after peroxone pretreatment.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 23.648 | 0.359 | 1.439 |
| 0.35 | 22.201 | 0.417 | 1.193 |
| 0.45 | 19.961 | 0.507 | 1.127 |
| 0.55 | 17.375 | 0.610 | 1.110 |
| 0.65 | 16.434 | 0.648 | 0.997 |
| 1.05 | 12.752 | 0.795 | 0.757 |
| 1.15 | 12.407 | 0.809 | 0.703 |
| Blank | 32.212 | | |

Initial TNT concentration (Co) = 32.645 mg/l          Volume (V) = 0.04

Table B.26. Adsorption isotherm data for TNT peat moss after peroxone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 23.776 | 0.438 | 2.921 |
| 0.25 | 20.920 | 0.552 | 2.210 |
| 0.35 | 17.030 | 0.708 | 2.023 |
| 0.45 | 15.306 | 0.777 | 1.726 |
| 0.55 | 13.010 | 0.868 | 1.579 |
| Blank | 36.464 | | |

Initial TNT concentration (Co) = 34.733 mg/l          Volume (V) = 0.04 l

Table B.27. Adsorption isotherm data for TNT raw peanut hulls after peroxone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 27.116 | 0.241 | 0.966 |
| 0.35 | 25.076 | 0.323 | 0.923 |
| 0.45 | 23.794 | 0.374 | 0.832 |
| 0.55 | 22.489 | 0.426 | 0.775 |
| 0.65 | 21.830 | 0.453 | 0.697 |
| 1.05 | 18.086 | 0.602 | 0.574 |
| 1.15 | 17.355 | 0.632 | 0.549 |
| Blank | 31.967 | | |

Initial TNT concentration (Co) = 33.159 mg/l          Volume (V) = 0.04 l

Table B.28. Adsorption isotherm data for TNT crushed peanut hulls after peroxone pretreatment.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 30.248 | 0.354 | 1.418 |
| 0.35 | 29.191 | 0.396 | 1.134 |
| 0.45 | 27.048 | 0.482 | 1.072 |
| 0.55 | 25.673 | 0.537 | 0.977 |
| 0.65 | 23.938 | 0.607 | 0.934 |
| 0.85 | 21.145 | 0.718 | 0.845 |
| 1.05 | 20.593 | 0.740 | 0.705 |
| 1.15 | 18.845 | 0.810 | 0.705 |
| Blank | 39.822 | | |

Initial TNT concentration (Co) = 39.116 mg/l          Volume (V) = 0.04 l

Table B.29. Adsorption isotherm data for TNT kenaf core after 2 hours of ultrasound pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 28.402 | 0.413 | 2.757 |
| 0.25 | 27.043 | 0.467 | 1.871 |
| 0.35 | 23.016 | 0.629 | 1.797 |
| 0.45 | 21.153 | 0.703 | 1.563 |
| 0.55 | 19.522 | 0.768 | 1.397 |
| 0.65 | 17.529 | 0.848 | 1.305 |
| 0.75 | 16.383 | 0.894 | 1.192 |
| Blank | 38.323 | | |

Initial TNT concentration (Co) = 38.742 mg/l          Volume (V) = 0.04 l


Table B.30. Adsorption isotherm data for TNT kenaf core after 2 hours of combination of ultrasound and ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 24.235 | 0.282 | 1.885 |
| 0.25 | 22.816 | 0.339 | 1.358 |
| 0.35 | 20.568 | 0.429 | 1.227 |
| 0.45 | 19.245 | 0.482 | 1.072 |
| 0.55 | 17.542 | 0.550 | 1.001 |
| 0.65 | 16.642 | 0.586 | 0.902 |
| 0.75 | 15.309 | 0.639 | 0.853 |
| Blank | 31.026 | | |

Initial TNT concentration (Co) = 31.307 mg/l          Volume (V) = 0.04 l

Table B.31. Adsorption isotherm data for TNT kenaf core after 4 hours of combination of ultrasound and ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 24.867 | 0.257 | 1.717 |
| 0.25 | 21.765 | 0.381 | 1.526 |
| 0.35 | 20.981 | 0.413 | 1.180 |
| 0.45 | 18.986 | 0.492 | 1.095 |
| 0.55 | 17.536 | 0.550 | 1.001 |
| 0.65 | 15.888 | 0.616 | 0.948 |
| 0.75 | 14.623 | 0.667 | 0.889 |
| Blank | 31.340 | | |

Initial TNT concentration (Co) = 31.307 mg/l          Volume (V) = 0.04 l

Table B.32. Adsorption isotherm data for TNT on peat moss after 2 hours of combination of ultrasound and ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 21.968 | 0.334 | 2.231 |
| 0.25 | 19.127 | 0.448 | 1.793 |
| 0.35 | 16.593 | 0.549 | 1.570 |
| 0.45 | 14.908 | 0.617 | 1.371 |
| 0.55 | 13.246 | 0.683 | 1.242 |
| 0.65 | 11.968 | 0.734 | 1.130 |
| 0.75 | 10.864 | 0.778 | 1.038 |
| Blank | 30.148 | | |

Initial TNT concentration (Co) = 30.335 mg/l          Volume (V) = 0.04 l

Table B.33. Adsorption isotherm data for TNT on peat moss after 4 hours of combination of ultrasound and ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 28.288 | 0.414 | 2.761 |
| 0.25 | 24.606 | 0.561 | 2.246 |
| 0.35 | 21.878 | 0.670 | 1.916 |
| 0.45 | 19.117 | 0.781 | 1.735 |
| 0.55 | 18.068 | 0.823 | 1.496 |
| 0.65 | 16.410 | 0.889 | 1.368 |
| 0.75 | 14.373 | 0.970 | 1.294 |
| Blank | 38.648 | | |

Initial TNT concentration (Co) = 38.645 mg/l          Volume (V) = 0.04 l

Table B.34. Adsorption isotherm data for TNT on raw peanut hulls after 2 hours of combination of ultrasound and ozone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 33.492 | 0.204 | 1.364 |
| 0.25 | 32.472 | 0.245 | 0.982 |
| 0.35 | 31.015 | 0.303 | 0.868 |
| 0.45 | 28.949 | 0.386 | 0.858 |
| 0.55 | 26.969 | 0.465 | 0.846 |
| 0.65 | 25.839 | 0.510 | 0.785 |
| Blank | 38.139 | | |

Initial TNT concentration (Co) = 38.611 mg/l          Volume (V) = 0.04 l

Table B.35. Adsorption isotherm data for TNT on raw peanut hulls after 4 hours of combination of ultrasound and ozone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of TNT Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 35.005 | 0.122 | 0.816 |
| 0.25 | 32.256 | 0.232 | 0.929 |
| 0.35 | 31.021 | 0.281 | 0.805 |
| 0.45 | 29.629 | 0.337 | 0.750 |
| 0.55 | 29.128 | 0.357 | 0.650 |
| 0.65 | 27.779 | 0.411 | 0.633 |
| 0.85 | 24.531 | 0.541 | 0.636 |
| 1.05 | 22.167 | 0.635 | 0.605 |
| 1.15 | 21.179 | 0.675 | 0.587 |
| Blank | 37.759 | | |

Initial TNT concentration (Co) = 38.066 mg/l          Volume (V) = 0.04 l

Table B.36. Adsorption isotherm data for 2,4-DCP on kenaf core.

| Mass of Kenaf Core (M), mg | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 3.491 | 0.060 | 0.404 |
| 0.25 | 3.078 | 0.077 | 0.308 |
| 0.35 | 2.646 | 0.094 | 0.269 |
| 0.45 | 2.308 | 0.108 | 0.240 |
| 0.55 | 2.036 | 0.118 | 0.216 |
| 0.65 | 1.787 | 0.128 | 0.198 |
| 0.75 | 1.600 | 0.136 | 0.181 |
| Blank | 4.982 | | |

Initial 2,4-DCP concentration (Co) = 5.008 mg/l          Volume (V) = 0.04 l

Table B.37. Adsorption isotherm data for 2,4-DCP on kenaf core.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 19.123 | 0.081 | 1.624 |
| 0.15 | 17.112 | 0.161 | 1.077 |
| 0.25 | 14.312 | 0.273 | 1.094 |
| 0.35 | 13.051 | 0.324 | 0.926 |
| 0.45 | 11.272 | 0.395 | 0.878 |
| 0.55 | 10.671 | 0.419 | 0.762 |
| 0.65 | 9.798 | 0.454 | 0.698 |
| 0.75 | 8.954 | 0.488 | 0.650 |
| Blank | 21.613 | | |

Initial 2,4-DCP concentration (Co) = 21.155 mg/l          Volume (V) = 0.04 l

Table B.38. Adsorption isotherm data for 2,4-DCP on kenaf stalk.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 3.145 | 0.052 | 0.346 |
| 0.45 | 1.958 | 0.099 | 0.221 |
| 0.55 | 1.832 | 0.104 | 0.190 |
| 0.65 | 1.639 | 0.112 | 0.172 |
| 0.75 | 1.564 | 0.115 | 0.153 |
| Blank | 4.259 | | |

Initial 2,4-DCP concentration (Co) = 4.445 mg/l          Volume (V) = 0.04 l

Table B.39. Adsorption isotherm data for 2,4-DCP on kenaf stalk.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 12.3 | 0.176 | 1.173 |
| 0.25 | 10.235 | 0.258 | 1.034 |
| 0.35 | 8.859 | 0.313 | 0.896 |
| 0.45 | 7.568 | 0.365 | 0.811 |
| 0.55 | 7.46 | 0.369 | 0.672 |
| 0.75 | 5.792 | 0.436 | 0.581 |
| Blank | 16.681 | | |

Initial 2,4-DCP concentration (Co) = 16.702 mg/l          Volume (V) = 0.04 l

Table B.40. Adsorption isotherm data for 2,4-DCP on peat moss

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 3.154 | 0.027 | 0.546 |
| 0.15 | 2.884 | 0.038 | 0.254 |
| 0.25 | 2.144 | 0.067 | 0.270 |
| 0.35 | 1.847 | 0.079 | 0.227 |
| 0.45 | 1.427 | 0.096 | 0.214 |
| 0.55 | 1.180 | 0.106 | 0.193 |
| 0.65 | 1.043 | 0.111 | 0.171 |
| 0.75 | 0.828 | 0.120 | 0.160 |
| Blank | 3.989 | | |

.Initial 2,4-DCP concentration (Co) = 3.837 mg/l          Volume (V) = 0.04 l

Table B.41. Adsorption isotherm data for 2,4-DCP on peat moss.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.05 | 18.256 | 0.094 | 1.892 |
| 0.15 | 15.181 | 0.216 | 1.441 |
| 0.25 | 12.903 | 0.300 | 1.202 |
| 0.35 | 11.225 | 0.383 | 1.094 |
| 0.55 | 8.354 | 0.481 | 0.874 |
| 0.65 | 7.270 | 0.519 | 0.799 |
| Blank | 20.420 | | |

Initial 2,4-DCP concentration (Co) = 20.622 mg/l          Volume (V) = 0.04Table

B.42. Adsorption isotherm data for 2,4-DCP on raw peanut hulls.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 10.659 | 0.180 | 1.202 |
| 0.25 | 8.432 | 0.269 | 1.077 |
| 0.35 | 6.6915 | 0.339 | 0.968 |
| 0.45 | 5.5485 | 0.384 | 0.854 |
| 0.55 | 4.535 | 0.425 | 0.773 |
| 0.65 | 4.547 | 0.424 | 0.653 |
| 0.75 | 3.132 | 0.481 | 0.641 |
| Blank | 14.59 | | |

Initial 2,4-DCP concentration (Co) = 15.167 mg/l          Volume (V) = 0.04 l

Table B.43. Adsorption isotherm data for 2,4-DCP on crushed peanut hulls.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 17.372 | 0.279 | 1.116 |
| 0.35 | 17.497 | 0.274 | 0.783 |
| 0.45 | 16.144 | 0.328 | 0.729 |
| 0.55 | 13.847 | 0.420 | 0.764 |
| 0.65 | 13.763 | 0.423 | 0.651 |
| 1.05 | 11.561 | 0.511 | 0.487 |
| 1.15 | 11.265 | 0.523 | 0.455 |
| Blank | 22.378 | | |

Initial 2,4-DCP concentration (Co) = 24.352 mg/l          Volume (V) = 0.04 l

Table B.44. Adsorption isotherm data for 2,4-DCP on hay.

| Mass of Hay (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 15.885 | 0.028 | 0.189 |
| 0.25 | 15.717 | 0.035 | 0.140 |
| 0.35 | 15.516 | 0.043 | 0.123 |
| 0.45 | 15.558 | 0.041 | 0.092 |
| 0.55 | 15.391 | 0.048 | 0.087 |
| 0.65 | 15.275 | 0.052 | 0.081 |
| 0.75 | 14.993 | 0.064 | 0.085 |
| Blank | 16.491 | | |

Initial 2,4-DCP concentration (Co) = 16.597 mg/l          Volume (V) = 0.04 l

Table B.45. Adsorption isotherm data for 2,4-DCP on kenaf core after 2 hours of ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 1.634 | 0.145 | 0.581 |
| 0.35 | 1.126 | 0.165 | 0.473 |
| 0.45 | 0.895 | 0.175 | 0.388 |
| 0.55 | 0.52 | 0.190 | 0.345 |
| Blank | 5.197 | | |

Initial 2,4-DCP concentration (Co) = 5.271 mg/l        Volume (V) = 0.04 l

Table B.46. Adsorption isotherm data for 2,4-DCP on kenaf stalk after 2 hours of ozone pretreatment.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 7.682 | 0.305 | 1.222 |
| 0.35 | 5.830 | 0.379 | 1.085 |
| 0.45 | 5.729 | 0.383 | 0.852 |
| 0.55 | 4.247 | 0.443 | 0.805 |
| 0.65 | 4.161 | 0.446 | 0.687 |
| Blank | 15.054 | | |

Initial 2,4-DCP concentration (Co) = 15.325 mg/l        Volume (V) = 0.04 l

Table B.47. Adsorption isotherm data for 2,4-DCP on peat moss after 2 hours of ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 6.526 | 0.341 | 1.364 |
| 0.35 | 5.245 | 0.392 | 1.120 |
| 0.45 | 4.074 | 0.439 | 0.975 |
| 0.55 | 2.858 | 0.487 | 0.886 |
| 0.65 | 1.97 | 0.523 | 0.805 |
| Blank | 14.683 | | |

Initial 2,4-DCP concentration (Co) = 15.054 mg/l          Volume (V) = 0.04 l

Table B.48. Adsorption isotherm data for 2,4-DCP on peat moss after 4 hours of ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 15.244 | 0.437 | 2.913 |
| 0.25 | 11.713 | 0.578 | 2.313 |
| 0.35 | 7.908 | 0.730 | 2.087 |
| 0.45 | 8.564 | 0.704 | 1.565 |
| 0.85 | 7.414 | 0.750 | 0.882 |
| 1.05 | 5.038 | 0.845 | 0.805 |
| 1.15 | 4.696 | 0.859 | 0.749 |
| Blank | 24.992 | | |

Initial 2,4-DCP concentration (Co) = 26.171 mg/l          Volume (V) = 0.04 l

Table B.49. Adsorption isotherm data for 2,4-DCP on raw peanut hulls after 2 hours of ozone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 11.568 | 0.149 | 0.993 |
| 0.35 | 8.395 | 0.276 | 0.788 |
| 0.55 | 6.109 | 0.367 | 0.668 |
| 0.75 | 4.999 | 0.411 | 0.549 |
| 0.95 | 4.446 | 0.433 | 0.456 |
| Blank | 13.792 | | |

Initial 2,4-DCP concentration (Co) = 15.295 mg/l          Volume (V) = 0.04 l

Table B.50. Adsorption isotherm data for 2,4-DCP on crushed peanut hulls after 2 hours of ozone pretreatment.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 7.147 | 0.320 | 2.134 |
| 0.25 | 6.264 | 0.355 | 1.422 |
| 0.35 | 5.736 | 0.376 | 1.076 |
| 0.45 | 4.068 | 0.443 | 0.985 |
| 0.55 | 4.198 | 0.438 | 0.796 |
| Blank | 13.442 | | |

Initial 2,4-DCP concentration (Co) = 15.152 mg/l          Volume (V) = 0.04 l

Table B.51. Adsorption isotherm data for 2,4-DCP on kenaf core after peroxone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 14.772 | 0.394 | 1.577 |
| 0.35 | 14.074 | 0.422 | 1.206 |
| 0.45 | 12.205 | 0.497 | 1.104 |
| 0.55 | 11.496 | 0.525 | 0.955 |
| 0.65 | 10.833 | 0.551 | 0.849 |
| 1.15 | 7.566 | 0.682 | 0.593 |
| Blank | 23.995 | | |

Initial 2,4-DCP concentration (Co) = 24.632 mg/l          Volume (V) = 0.04 l

Table B.52. Adsorption isotherm data for 2,4-DCP on peat moss after peroxone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.35 | 12.46 | 0.436 | 1.247 |
| 0.45 | 9.816 | 0.542 | 1.205 |
| 0.55 | 9.120 | 0.570 | 1.036 |
| 0.65 | 8.884 | 0.579 | 0.891 |
| Blank | 22.928 | | |

Initial 2,4-DCP concentration (Co) = 23.379 mg/l          Volume (V) = 0.04 l

Table B.53. Adsorption isotherm data for 2,4-DCP on kenaf stalk after peroxone pretreatment.

| Mass of Kenaf Stalk (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 16.867 | 0.109 | 0.436 |
| 0.35 | 15.993 | 0.144 | 0.411 |
| 0.45 | 15.312 | 0.171 | 0.380 |
| 0.65 | 13.786 | 0.232 | 0.357 |
| Blank | 19.236 | | |

Initial 2,4-DCP concentration (Co) = 19.593 mg/l          Volume (V) = 0.04 l

Table B.54. Adsorption isotherm data for 2,4-DCP on raw peanut hulls after peroxone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 16.015 | 0.264 | 1.059 |
| 0.35 | 14.817 | 0.312 | 0.893 |
| 0.55 | 12.570 | 0.402 | 0.732 |
| 0.85 | 9.137 | 0.540 | 0.635 |
| 1.15 | 7.211 | 0.617 | 0.536 |
| Blank | 20.998 | | |

Initial 2,4-DCP concentration (Co) = 22.639 mg/l          Volume (V) = 0.04 l

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Table B.55. Adsorption isotherm data for 2,4-DCP on crushed peanut hulls after peroxone pretreatment.

| Mass of Crushed Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 14.922 | 0.228 | 0.913 |
| 0.35 | 14.118 | 0.260 | 0.744 |
| 0.45 | 13.428 | 0.288 | 0.640 |
| 0.55 | 12.866 | 0.310 | 0.564 |
| Blank | 19.272 | | |

Initial 2,4-DCP concentration (Co) = 20.631 mg/l        Volume (V) = 0.04 l

Table B.56. Adsorption isotherm data for 2,4-DCP on kenaf core after a combination of ultrasound and ozone pretreatment.

| Mass of Kenaf Core (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 11.658 | 0.282 | 1.883 |
| 0.25 | 10.54 | 0.327 | 1.309 |
| 0.35 | 9.473 | 0.369 | 1.056 |
| 0.45 | 6.776 | 0.477 | 1.061 |
| 0.55 | 6.15 | 0.502 | 0.914 |
| Blank | 17.585 | | |

Initial 2,4-DCP concentration (Co) = 18.721 mg/l        Volume (V) = 0.04 l

Table B.57. Adsorption isotherm data for 2,4-DCP on peat moss after ultrasound pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 12.457 | 0.441 | 1.766 |
| 0.45 | 11.237 | 0.490 | 1.089 |
| 0.55 | 9.767 | 0.549 | 0.998 |
| 0.65 | 8.576 | 0.596 | 0.918 |
| 1.05 | 6.999 | 0.659 | 0.628 |
| Blank | 23.079 | | |

Initial 2,4-DCP concentration (Co) = 23.495 mg/l          Volume (V) = 0.04 l

Table B.58. Adsorption isotherm data for 2,4-DCP on peat moss after 2 hours of combination of ultrasound and ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 14.897 | 0.463 | 3.092 |
| 0.25 | 14.309 | 0.487 | 1.949 |
| 0.35 | 10.198 | 0.651 | 1.862 |
| 0.45 | 9.244 | 0.689 | 1.533 |
| 0.55 | 9.043 | 0.698 | 1.269 |
| 0.65 | 7.300 | 0.767 | 1.181 |
| 0.85 | 6.066 | 0.817 | 0.961 |
| 1.15 | 5.391 | 0.844 | 0.733 |
| Blank | 23.995 | | |

Initial 2,4-DCP concentration (Co) = 26.493 mg/l          Volume (V) = 0.04 l

Table B.59. Adsorption isotherm data for 2,4-DCP on peat moss after 4 hours of combination of ultrasound and ozone pretreatment.

| Mass of Peat Moss (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.25 | 11.185 | 0.451 | 1.804 |
| 0.35 | 9.130 | 0.533 | 1.523 |
| 0.45 | 7.982 | 0.579 | 1.287 |
| 0.55 | 7.865 | 0.583 | 1.061 |
| 0.65 | 7.186 | 0.611 | 0.940 |
| 0.85 | 5.666 | 0.671 | 0.790 |
| 1.05 | 5.725 | 0.669 | 0.637 |
| 1.15 | 4.626 | 0.713 | 0.620 |
| Blank | 23.716 | | |

Initial 2,4-DCP concentration (Co) = 22.463 mg/l          Volume (V) = 0.04 l

Table B.60. Adsorption isotherm data for 2,4-DCP on raw peanut hulls after 2 hours of combination of ultrasound and ozone pretreatment.

| Mass of Raw Peanut Hulls (M), gm | Residual Concentration (Cf), mg/l | Mass of 2,4-DCP Adsorbed (X), mg | X/M, mg/gm |
|---|---|---|---|
| 0.15 | 18.438 | 0.100 | 0.669 |
| 0.25 | 17.313 | 0.145 | 0.581 |
| 0.45 | 14.147 | 0.272 | 0.604 |
| 0.55 | 12.833 | 0.324 | 0.590 |
| 0.65 | 12.534 | 0.336 | 0.517 |
| 0.85 | 11.114 | 0.393 | 0.462 |
| 1.05 | 9.416 | 0.461 | 0.439 |
| 1.15 | 7.73 | 0.528 | 0.459 |
| Blank | 20.827 | | |

Initial 2,4-DCP concentration (Co) = 20.947 mg/l          Volume (V) = 0.04 l

Table B.61. Comparison of adsorption capacity (mg/gm) on TNT adsorption after ozone pretreatment at different equilibrium concentrations..

| Adsorbent | 10 : g/l (TNT) | | 10 mg/l (TNT) | |
|---|---|---|---|---|
| | Untreated | Ozonated (2 hours) | Untreated | Ozonated (2 hours) |
| Kenaf core | 0.00014 | 0.01128 | 0.43 | 0.737 |
| Kenaf stalk | 0.0066 | 0.1029 | 1.29 | 1.055 |
| Peat moss | 0.035 | 0.171 | 1.24 | 0.958 |
| Raw peanut hulls | 0.00006 | 0.0 | 0.180 | 0.06 |
| Crushed peanut hulls | 0.0172 | 0.0 | 0.88 | 0.27 |

Table B.62. Comparison of adsorption capacity (mg/gm) on 2,4-DCP adsorption after ozone pretreatment at different equilibrium concentrations.

| Adsorbent | 10 : g/l (2,4-DCP) | | 10 mg/l (2,4-DCP) | |
|---|---|---|---|---|
| | Untreated | Ozonated (2 hours) | Untreated | Ozonated (2 hours) |
| Kenaf core | 0.0015 | 0.0528 | 1.07 | 1.26 |
| Kenaf stalk | 0.0018 | 0.0048 | 0.97 | 1.48 |
| Peat moss | 0.0019 | 0.087 | 0.923 | 1.49 |
| Raw peanut hulls | 0.024 | 0.0045 | 1.16 | 0.863 |
| Crushed peanut hulls | 0.000012 | 0.00022 | 0.40 | 2.87 |

Table B.63. Comparison of adsorption capacity (mg/gm) on TNT adsorption after peroxone pretreatment at different equilibrium concentrations.

| Adsorbent | 10 : g/l (TNT) | | 10 mg/l (TNT) | |
|---|---|---|---|---|
| | Untreated | Peroxone | Untreated | Peroxone |
| Kenaf core | 0.00014 | 0.0 | 0.436 | 0.430 |
| Kenaf stalk | 0.0066 | 0.0007 | 1.29 | 0.593 |
| Peat moss | 0.035 | 0.0015 | 1.24 | 1.18 |
| Raw peanut hulls | 0.00006 | 0.00002 | 0.180 | 0.25 |
| Crushed peanut hulls | 0.0172 | 0.00002 | 0.88 | 0.278 |

Table B.64. Comparison of adsorption capacity (mg/gm) on 2,4-DCP adsorption after peroxone pretreatment at different equilibrium concentrations.

| Adsorbent | 10 : g/l (2,4-DCP) | | 10 mg/l (2,4-DCP) | |
|---|---|---|---|---|
| | Untreated | Peroxone | Untreated | Peroxone |
| Kenaf core | 0.00047 | 0.00007 | 0.673 | 0.83 |
| Kenaf stalk | 0.0018 | 0.0002 | 0.97 | 0.25 |
| Peat moss | 0.0019 | 0.0044 | 0.95 | 1.04 |
| Raw peanut hulls | 0.024 | 0.0033 | 1.16 | 0.67 |
| Crushed peanut hulls | 0.000012 | 0.0 | 0.40 | 0.248 |

Table B.65. Comparison of adsorption capacity (mg/gm) on TNT adsorption after combination of ultrasound and ozone pretreatment at different equilibrium concentrations.

| Adsorbent | 10 : g/l | | 10 mg/l (TNT) | |
|---|---|---|---|---|
| | Untreated | Ultrasound-ozone (2 hours) | Untreated | Ultrasound-ozone (2 hours) |
| Kenaf core | 0.00014 | 0.0 | 0.43 | 0.40 |
| Peat moss | 0.035 | 0.0006 | 1.24 | 0.91 |
| Raw peanut hulls | 0.00006 | 0.0042 | 0.18 | 0.42 |

Table B.66. Comparison of adsorption capacity (mg/gm) on 2,4-DCP adsorption after combination of ultrasound and ozone pretreatment at different equilibrium concentrations.

| Adsorbent | 10 : g/l (2,4-DCP) | | 10 mg/l (2,4-DCP) | |
|---|---|---|---|---|
| | Untreated | Ultrasound-ozone (2 hours) | Untreated | Ultrasound-ozone (2 hours) |
| Kenaf core | 0.00047 | 0.0039 | 0.67 | 1.31 |
| Peat moss | 0.0019 | 0.0005 | 0.95 | 1.58 |
| Raw peanut hulls | 0.024 | 0.019 | 1.16 | 0.46 |

Table B.67. Freundlich parameters for  kenaf core with TNT as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No Treatment | 0.030 | 1.163 | 0.835 |
| Ozonated (1Hour) | 0.024 | 1.274 | 0.815 |
| Ozonated (2 Hours) | 0.183 | 0.605 | 0.919 |
| Peroxone | 0.011 | 1.593 | 0.877 |
| Ultrasound (2 Hours) | 0.033 | 1.272 | 0.938 |
| Ultrasound-Ozone (2 Hours) | 0.011 | 1.560 | 0.956 |
| Ultrasound-Ozone (4 Hours) | 0.028 | 1.260 | 0.950 |

Table B.68. Freundlich parameters for kenaf stalk with TNT as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No Treatment | 0.223 | 0.764 | 0.876 |
| Ozonated (2Hours) | 0.486 | 0.337 | 0.531 |
| Peroxone | 0.063 | 0.974 | 0.974 |

Table B.69. Freundlich parameters for peat moss with TNT as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No Treatment | 0.379 | 0.517 | 0.956 |
| Ozonated (1 Hour) | 0.083 | 1.037 | 0.981 |
| Ozonated (2 Hours) | 0.540 | 0.249 | 0.848 |
| Ozonated (4 Hours) | 0.142 | 0.843 | 0.992 |
| Ultrasound - Ozone (2 Hours) | 0.080 | 1.060 | 0.994 |
| Ultrasound - Ozone (4 Hours) | 0.056 | 1.154 | 0.987 |
| Peroxone | 0.130 | 0.96 | 0.96 |

Table B.70. Freundlich parameters for raw peanut hulls with TNT as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No Treatment | 0.013 | 1.143 | 0.890 |
| Ozonated (2 Hours) | 0.0002 | 2.495 | 0.967 |
| Peroxone | 0.012 | 1.331 | 0.990 |
| Ultrasound-Ozone (2 Hours) | 0.091 | 0.667 | 0.957 |
| Ultrasound -Ozone (4 Hours) | 0.037 | 0.882 | 0.886 |

Table B.71. Freundlich parameters for crushed peanut hulls with TNT as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No Treatment | 0.238 | 0.570 | 0.887 |
| Ozonated (2 Hours) | 0.023 | 1.084 | 0.966 |
| Peroxone | 0.013 | 1.331 | 0.960 |

Table B.72. Freundlich parameters for kenaf core with 2,4-DCP as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation coefficient, r |
|---|---|---|---|
| No treatment $[DCP]_0 =$ 5 mg/lit | 0.12 | 0.95 | 0.99 |
| Ozonated (2 Hours) | 0.44 | 0.46 | 0.96 |
| No treatment $[DCP]_0 = 20$ mg/lit | 0.06 | 1.05 | 0.95 |
| Peroxone | 0.037 | 1.35 | 0.94 |
| Ultrasound-ozone (2 Hours) | 0.19 | 0.84 | 0.83 |

Table B.73. Freundlich parameters for kenaf stalk with 2,4-DCP as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation coefficient, r |
|---|---|---|---|
| No treatment | 0.12 | 0.91 | 0.99 |
| ozonated (2 Hours) | 0.22 | 0.83 | 0.91 |
| Peroxone | 0.026 | 0.99 | 0.97 |

Table B.74. Freundlich parameters for crushed peanut hulls with 2,4-DCP as the adsorbate

|  | K (mg/gm) | 1/n | Correlation coefficient, r |
|---|---|---|---|
| No treatment | 0.0124 | 1.5 | 0.89 |
| ozonated (2 Hours) | 0.121 | 1.37 | 0.89 |
| Peroxone | 0.00014 | 3.23 | 0.99 |

Table B.75. Freundlich parameters for peat moss with 2,4-DCP as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation Coefficient, r |
|---|---|---|---|
| No treatment | 0.12 | 0.9 | 0.99 |
| Ozonated (1 hour) | 0.019 | 1.96 | 0.91 |
| Ozonated (2 hours) | 0.58 | 0.41 | 0.96 |
| Ozonated (4 hours) | 0.11 | 1.21 | 0.91 |
| Peroxone | 0.17 | 0.79 | 0.79 |
| Ultrasound | 0.03 | 1.54 | 0.94 |
| Ultrasound-ozone (2 hours) | 0.11 | 1.16 | 0.95 |
| Ultrasound-ozone (4 hours) | 0.07 | 1.33 | 0.96 |

Table B.76. Freundlich parameters for raw peanut hulls with 2,4-DCP as the adsorbate.

|  | K (mg/gm) | 1/n | Correlation coefficient, r |
|---|---|---|---|
| No treatment | 0.32 | 0.56 | 0.96 |
| Ozonated (2 hours) | 0.15 | 0.76 | 0.98 |
| Peroxone | 0.113 | 0.766 | 0.97 |
| Ultrasound-ozone (2 hours) | 0.16 | 0.46 | 0.88 |

APPENDIX C

ADSORPTION ISOTHERM PLOTS
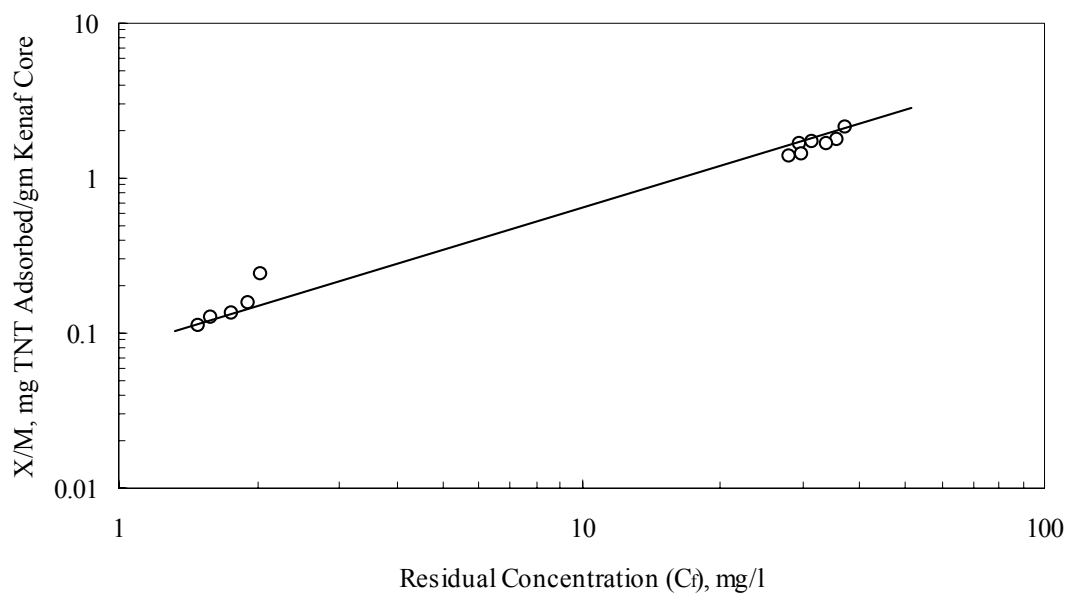
Figure C.1. Adsorption isotherm for TNT on kenaf core (Temperature = 25 $^0$ C, pH = 5).

Note : A logarithmic plot of X/M against $C_f$ yields a straight line (best fit). The slope is 1/n and the intercept at $C_f$ = 1 mg/l is k.
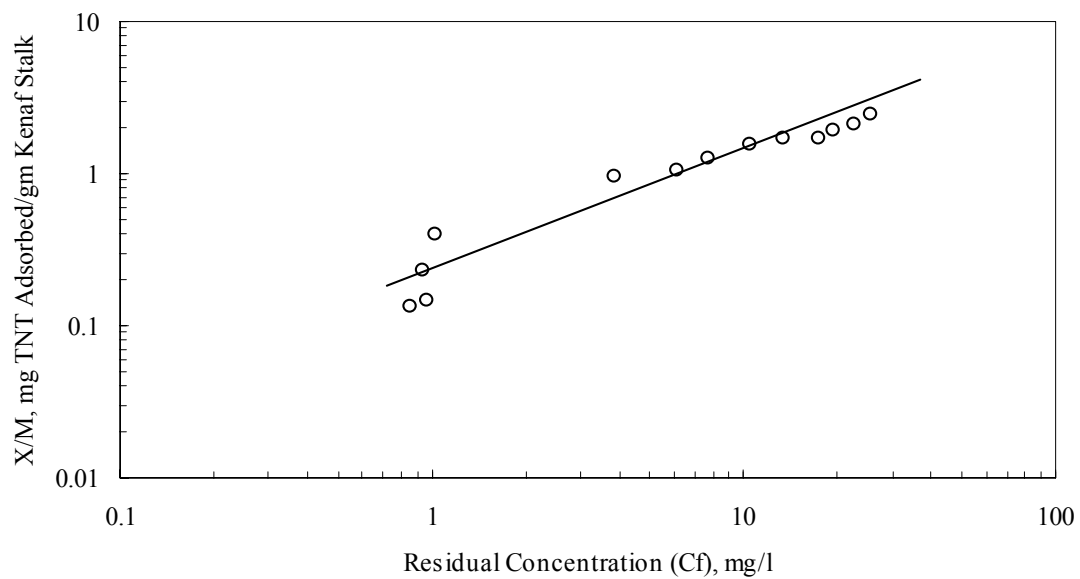
Figure C.2 . Adsorption isotherm for TNT on kenaf stalk (Temperature = 25 $^0$ C, pH = 5).
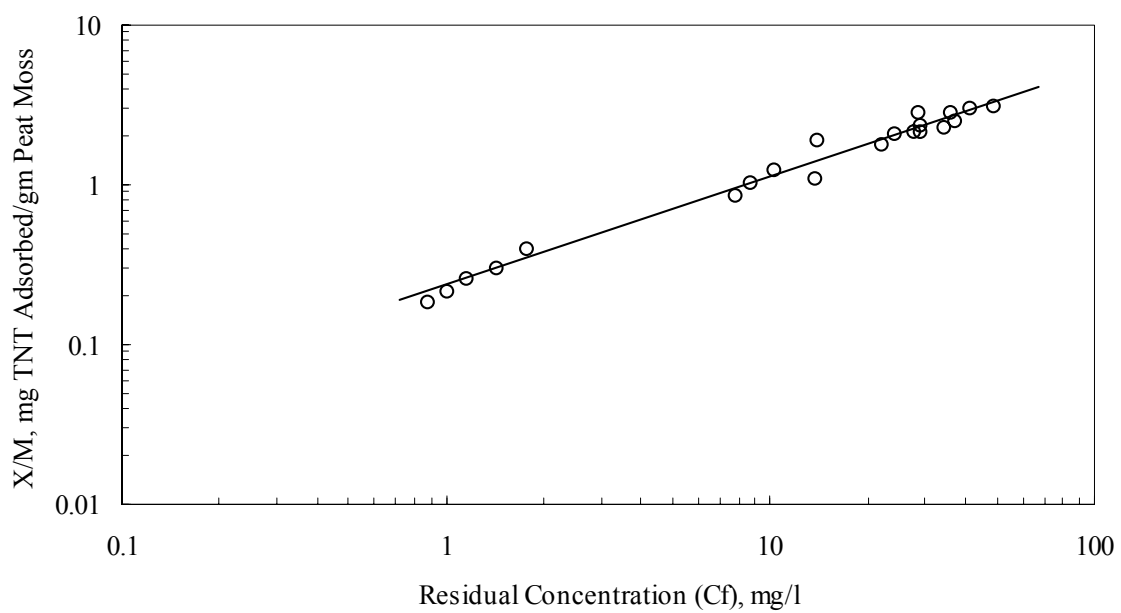
Figure C.3. Adsorption isotherm for TNT on peat moss (Temperature = 25 $^0$ C, pH = 5).
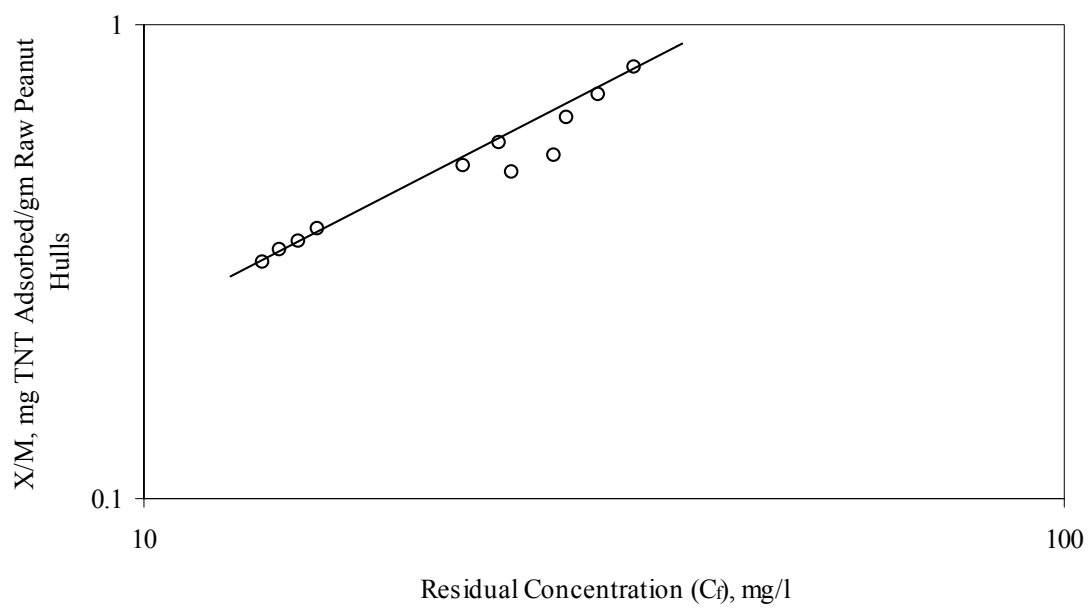
Figure C.4. Adsorption isotherm for TNT on raw peanut hulls (Temperature = 25 $^0$ C, pH = 5).
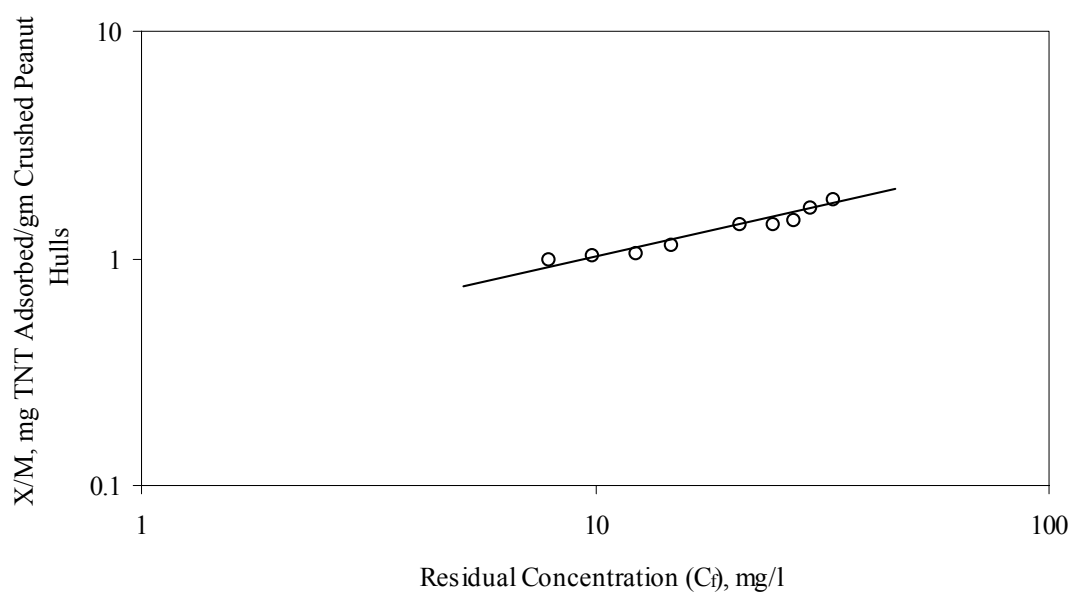
Figure C.5. Adsorption isotherm for TNT on crushed peanut hulls
(Temperature = 25 $^0$ C, pH = 5).
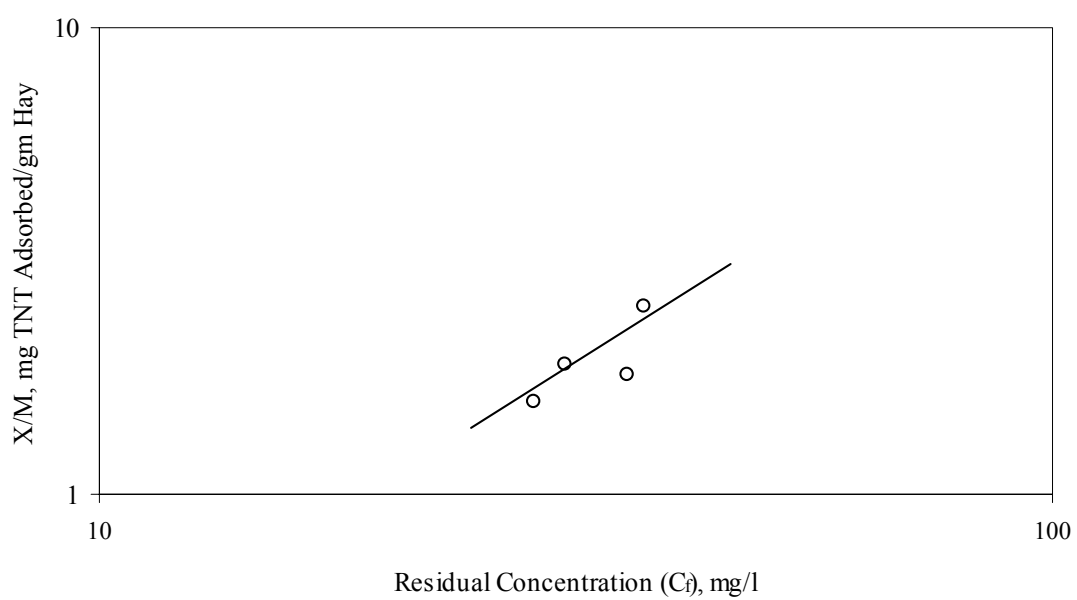
Figure C.6. Adsorption isotherm for TNT on hay (Temperature = $25\ ^0$ C, pH = 5).
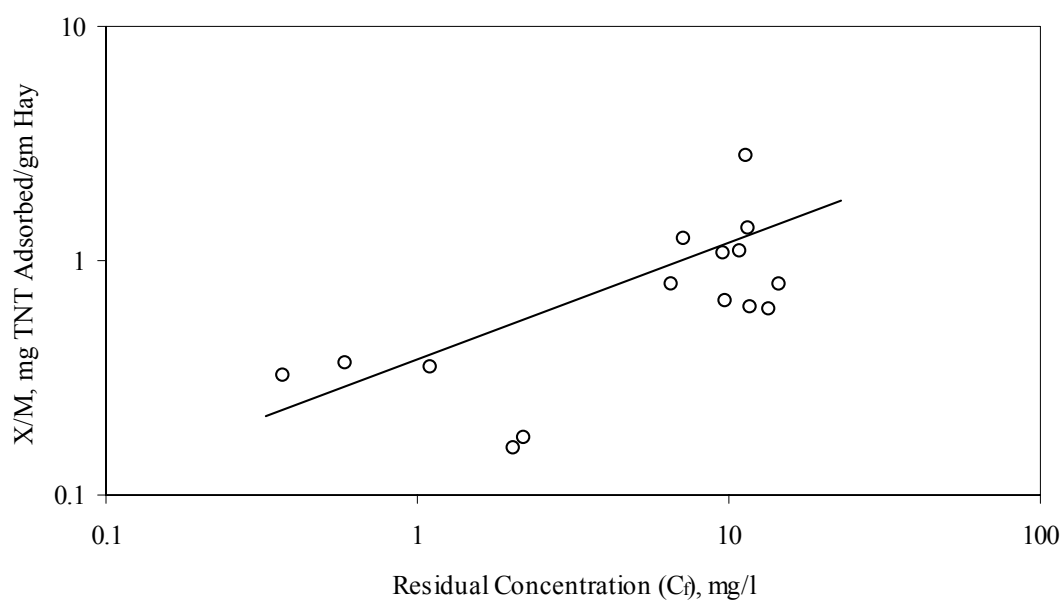
Figure C.7. Adsorption isotherm for TNT on hay (Temperature = 25 $^0$ C, pH = 5).
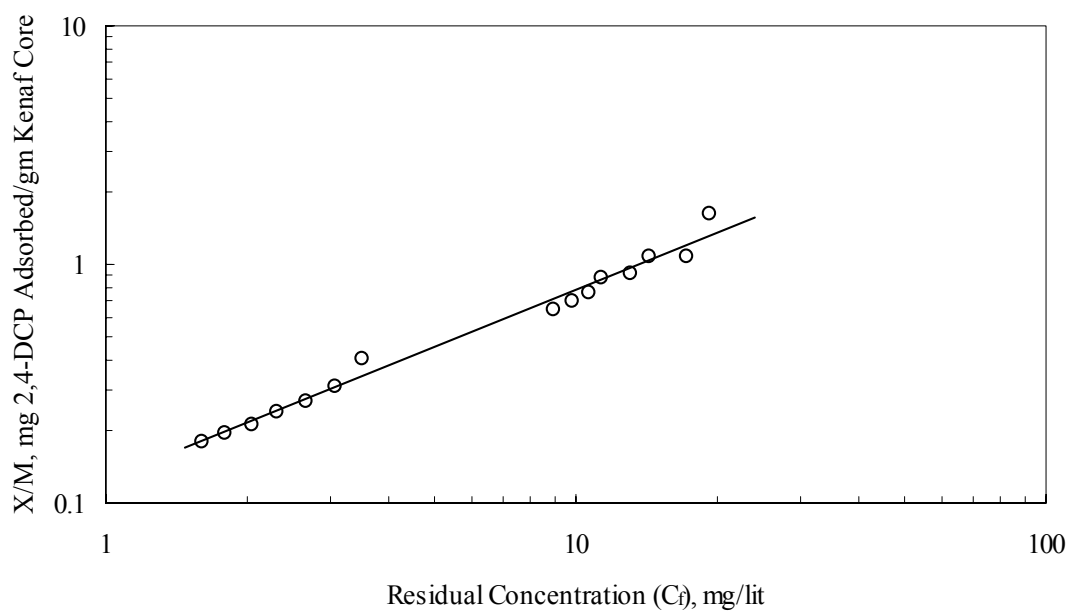
Figure C.8. Adsorption isotherm for 2,4-DCP on kenaf core (Temperature = 25 $^0$ C, pH = 5).
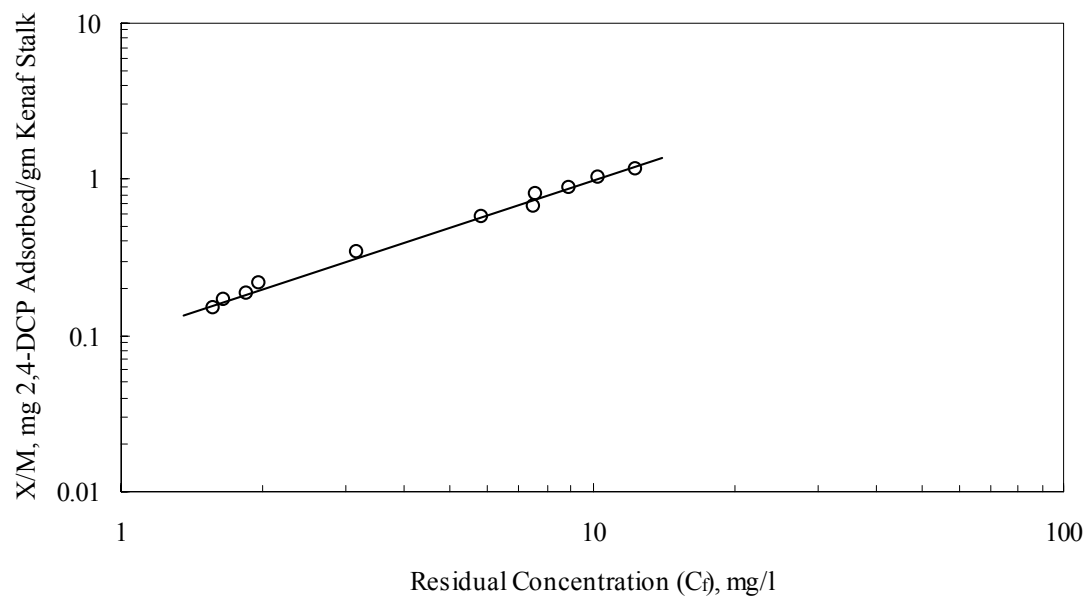
Figure C.9. Adsorption isotherm for 2,4-DCP on kenaf stalk (Temperature = 25 $^0$ C, pH = 5).
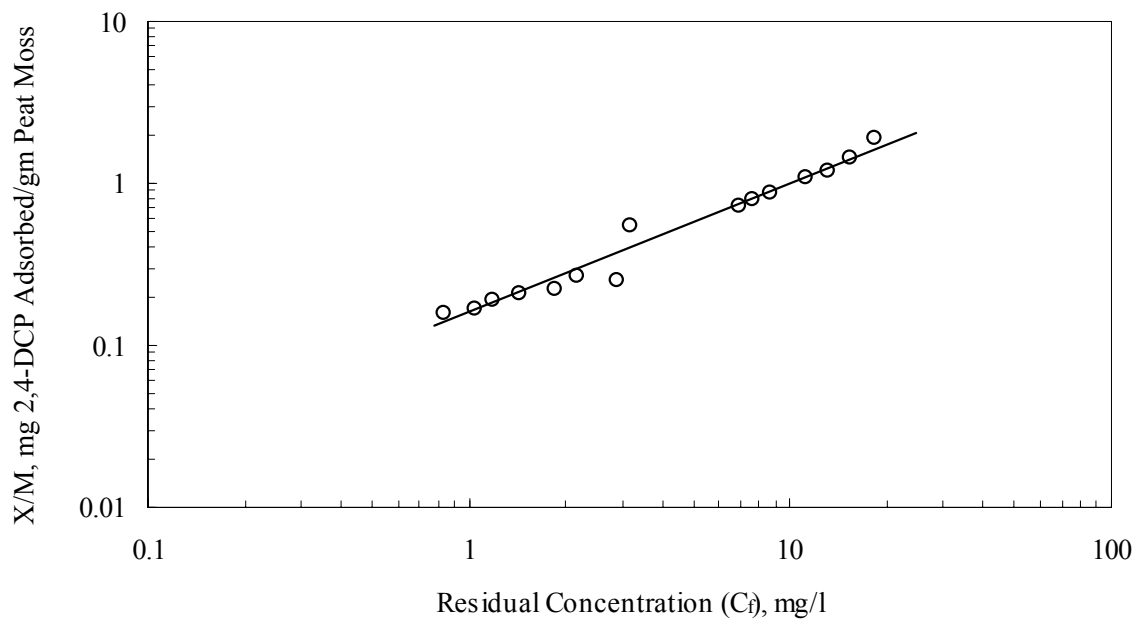
Figure C.10. Adsorption isotherm for 2,4-DCP on peat moss (Temperature = 25 $^0$ C, pH = 5).
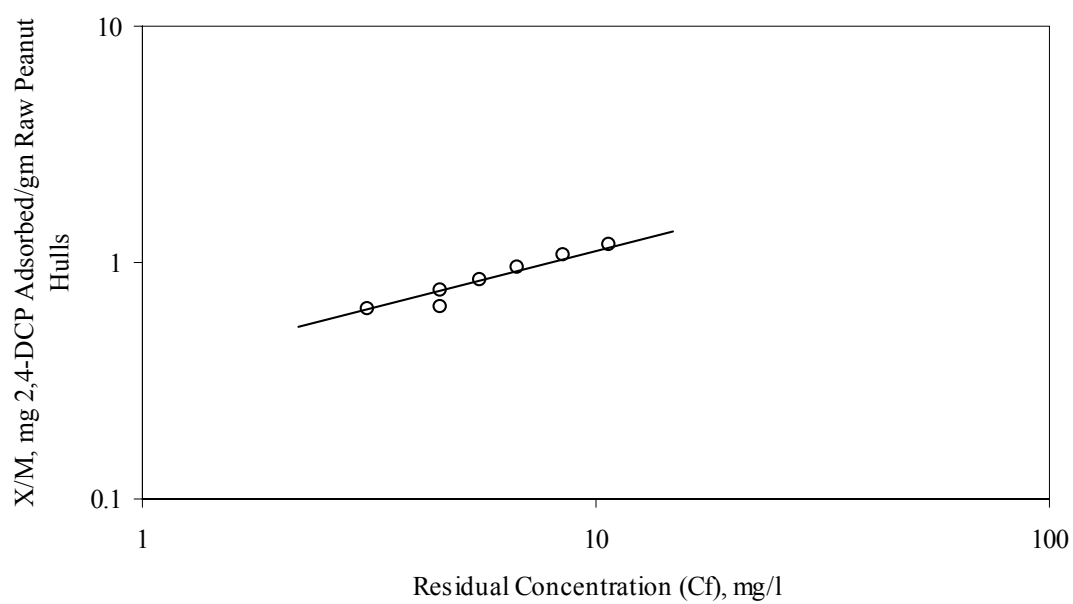
Figure C.11. Adsorption isotherm for 2,4-DCP on raw peanut hulls
(Temperature = 25 $^0$ C, pH = 5).
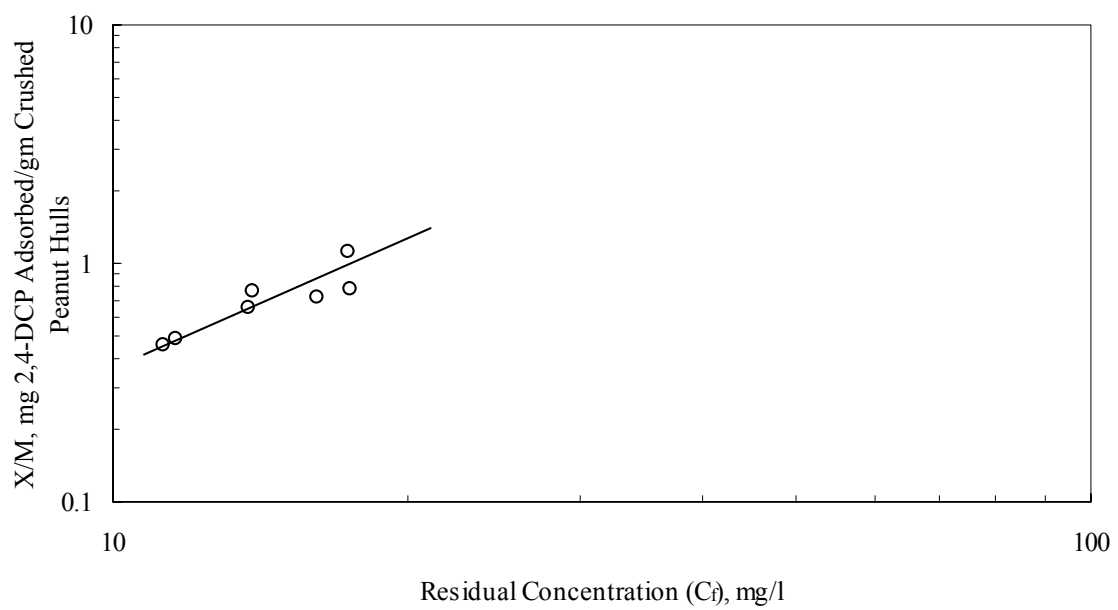
Figure C.12. Adsorption isotherm for 2,4-DCP on crushed peanut hulls
(Temperature = 25 $^0$ C, pH = 5).
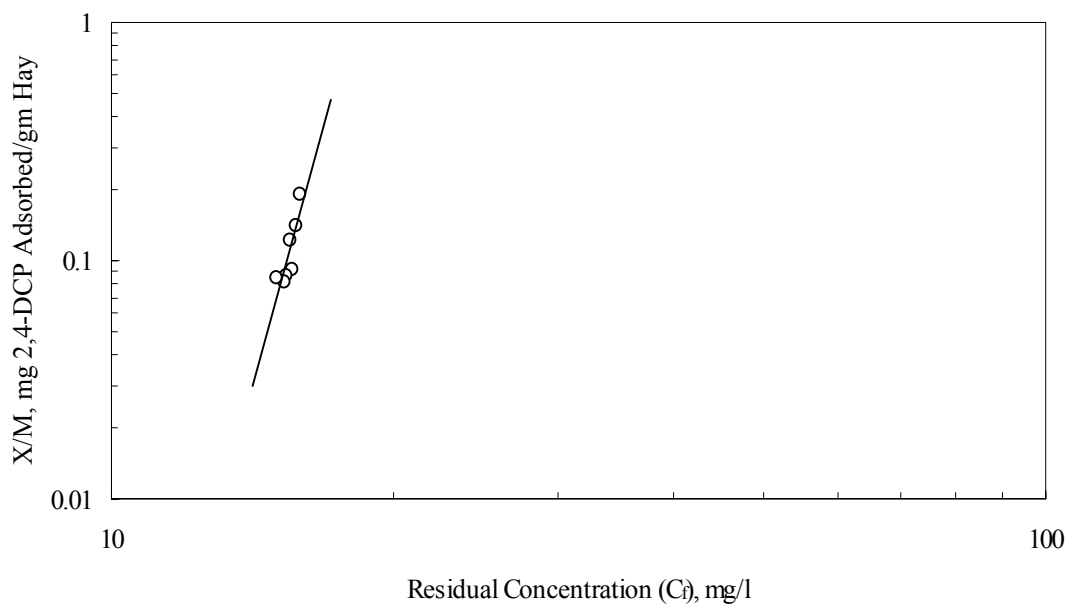
Figure C.13. Adsorption isotherm for 2,4-DCP on hay (Temperature = 25 $^0$ C, pH = 5).
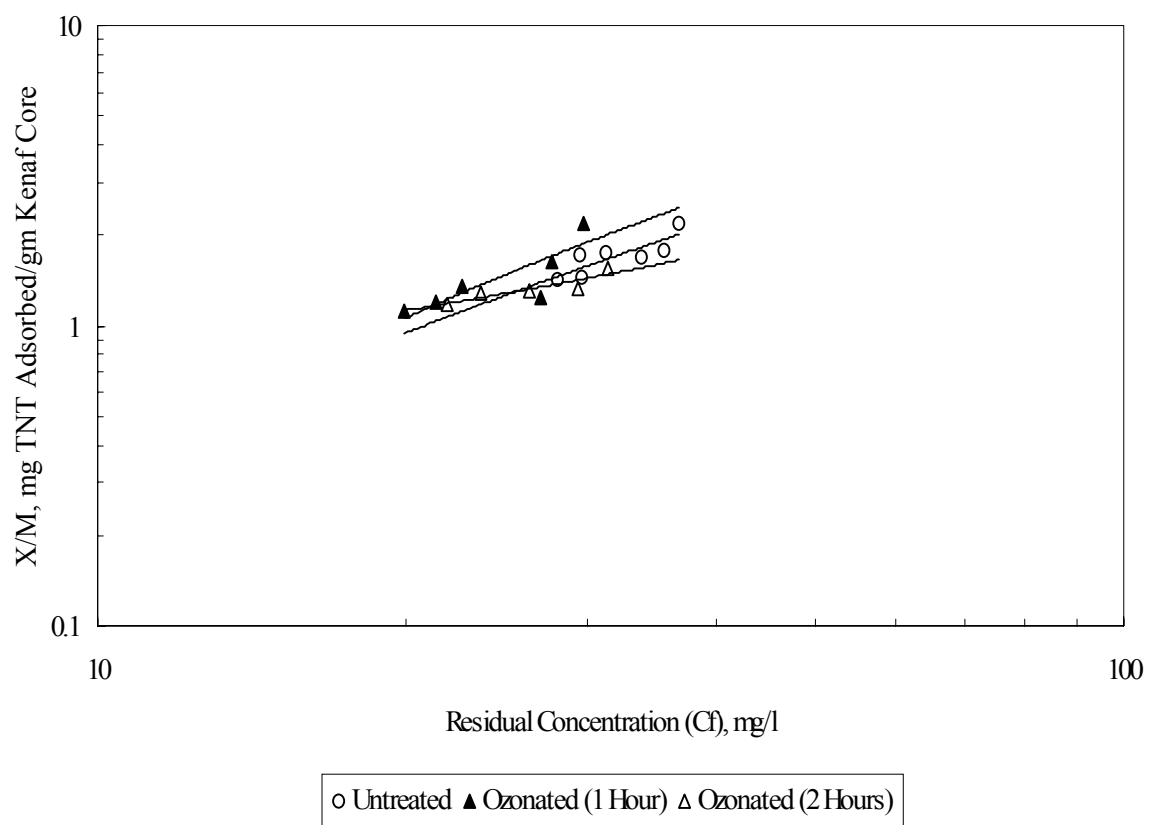
Figure C.14. Effect of ozone pretreatment of kenaf core on TNT adsorption
(Temperature = 25 $^0$ C).
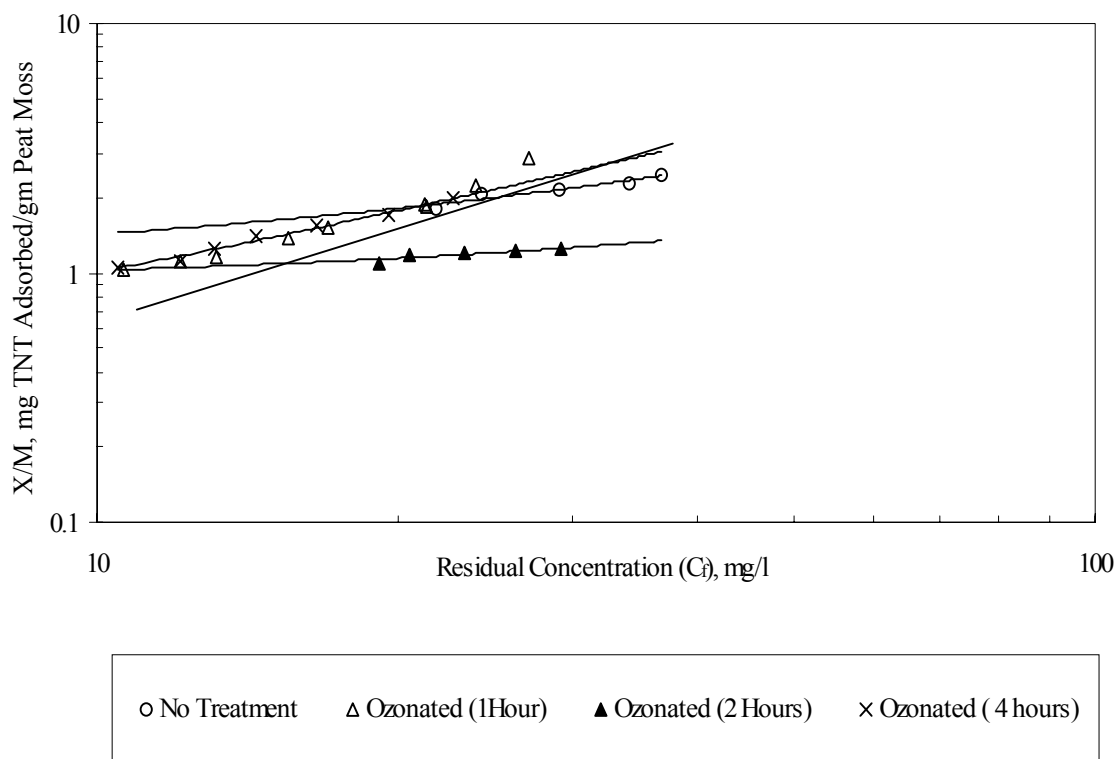
Figure C.15. Effect of ozone pretreatment of peat moss on the adsorption of TNT. (Temperature = 25 $^0$ C, pH = 5).
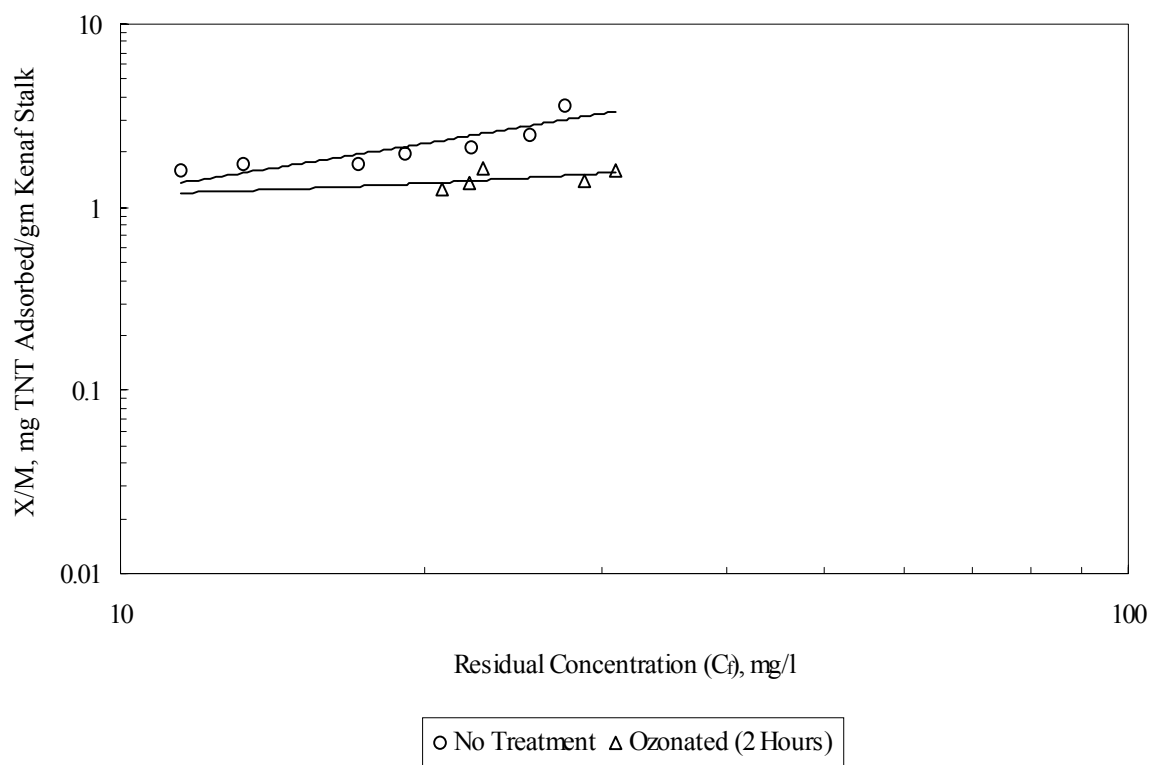
Figure C.16. Effect of pretreatment of kenaf stalk on TNT adsorption
(Temperature = 25 $^0$C, pH = 5).
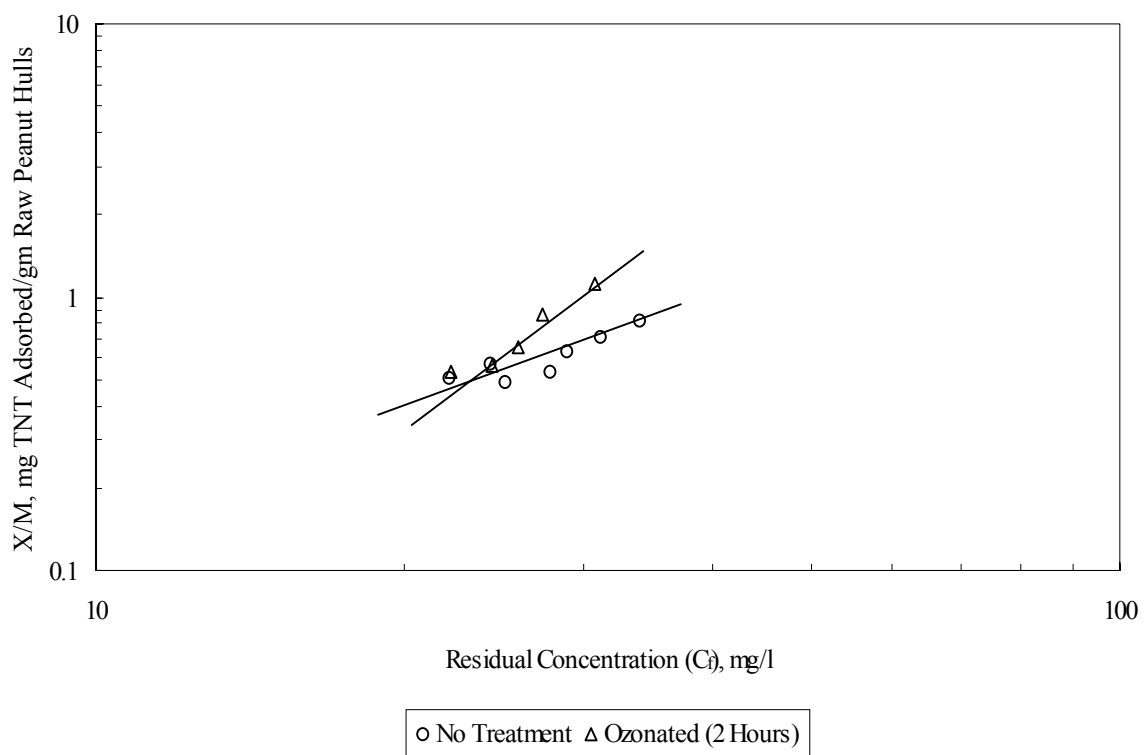
Figure C.17. Effect of ozone pretreatment of raw peanut hulls on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
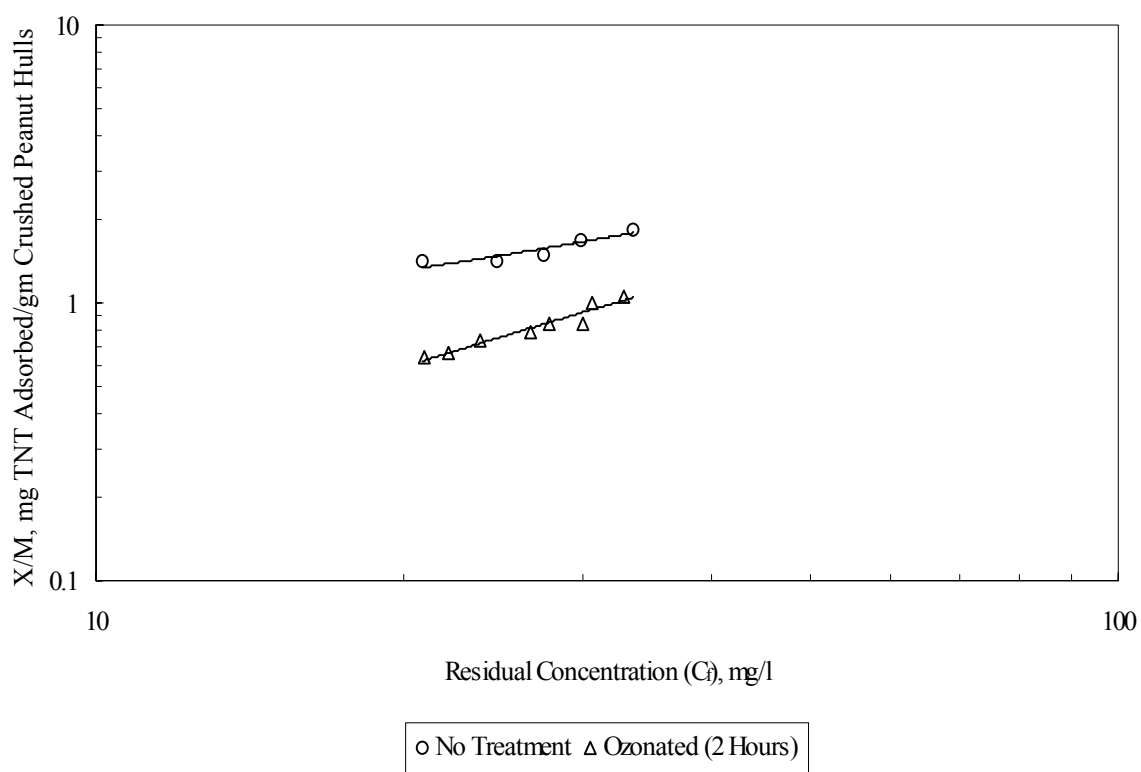
Figure C.18. Effect of ozone pretreatment of crushed peanut hulls on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
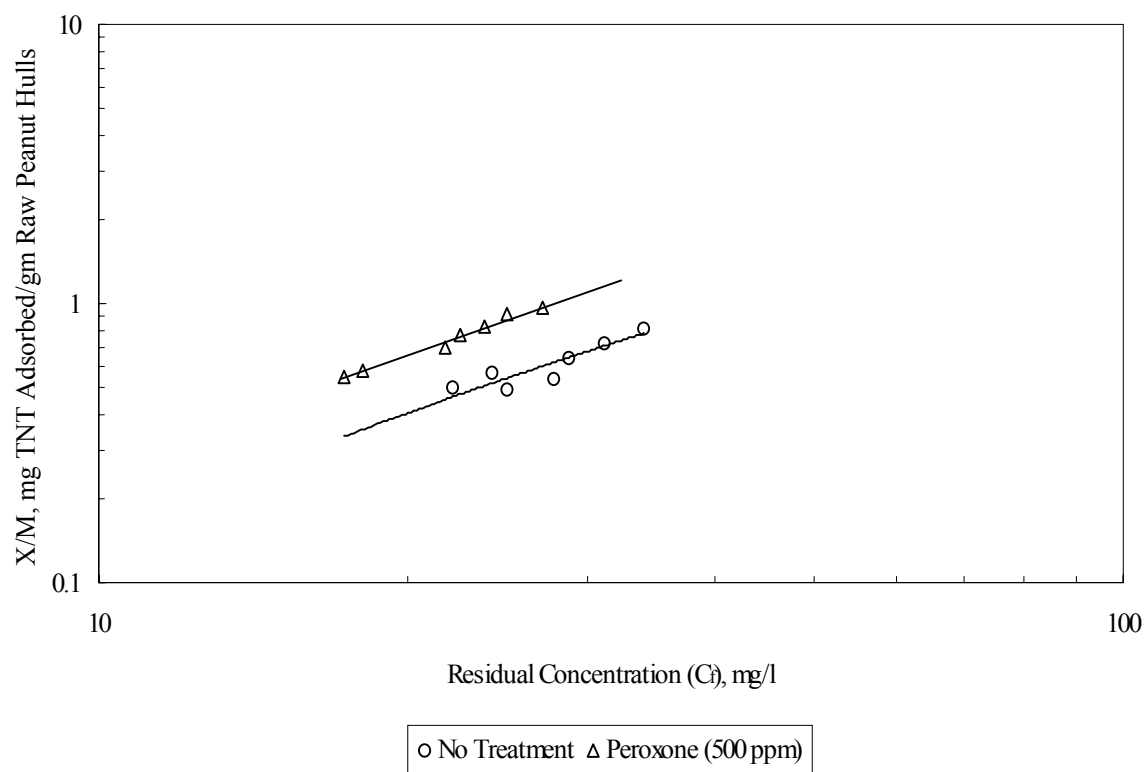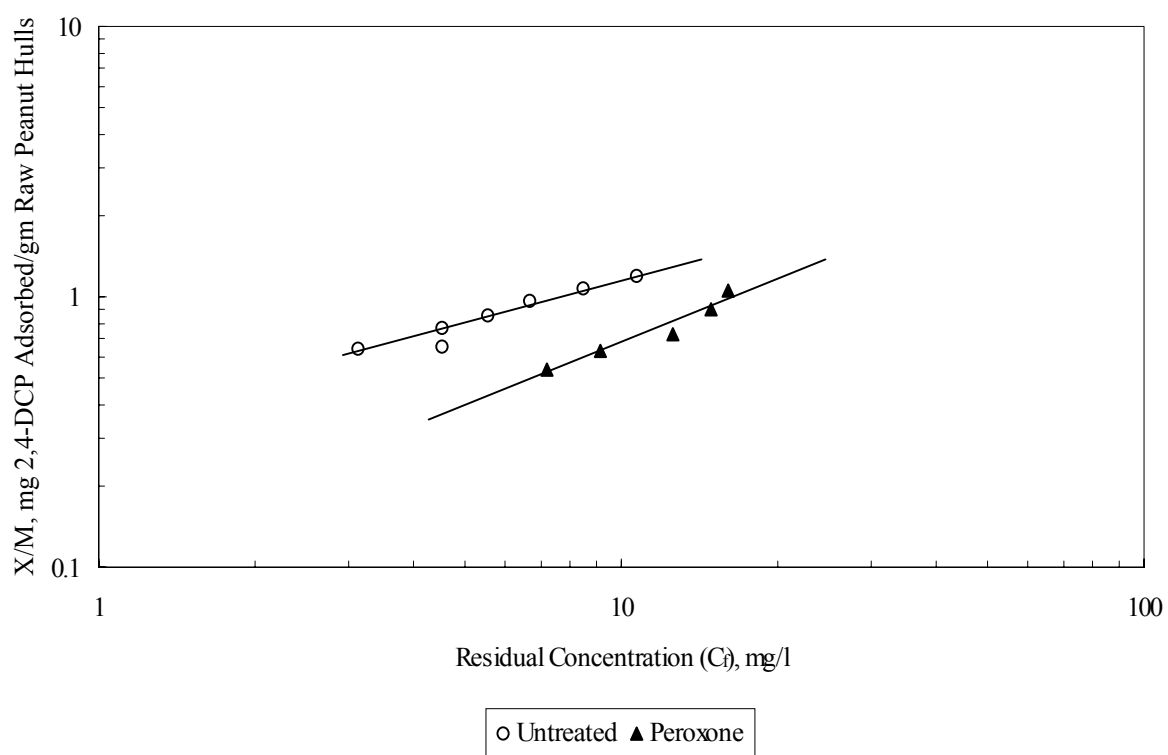
Figure C.19. Effect of peroxone pretreatment of raw peanut hulls on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
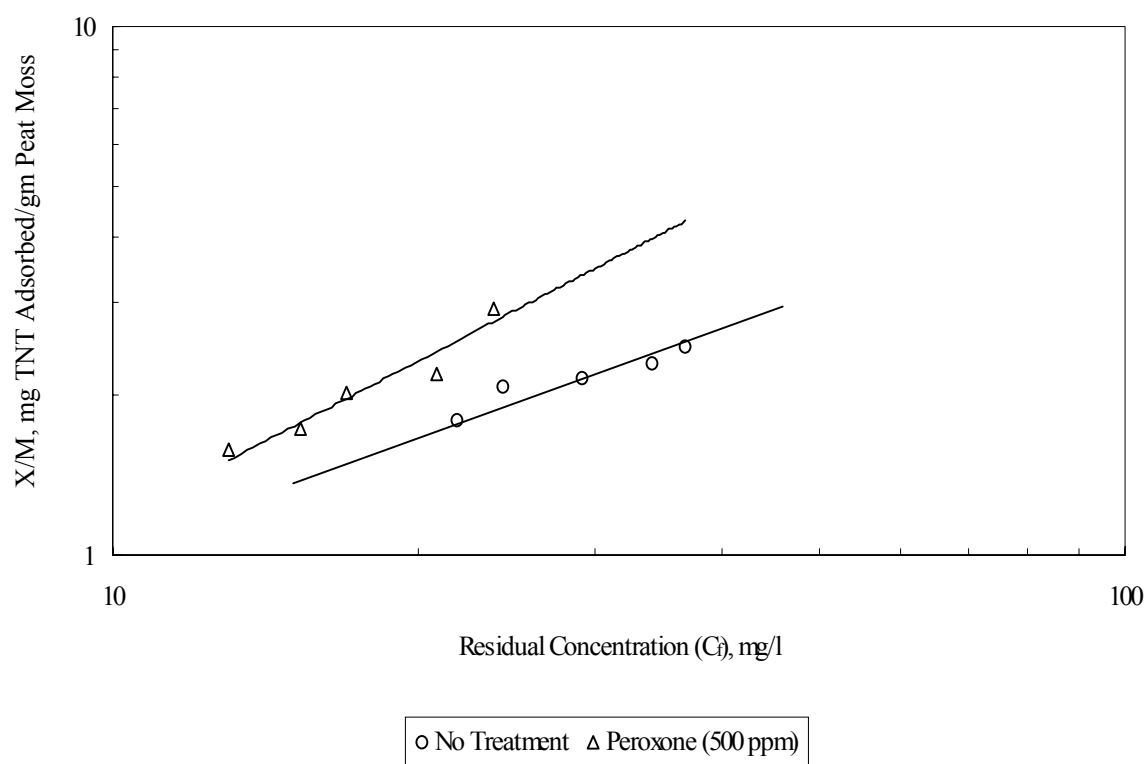
Figure C.20. Effect of peroxone pretreatment of peat moss on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
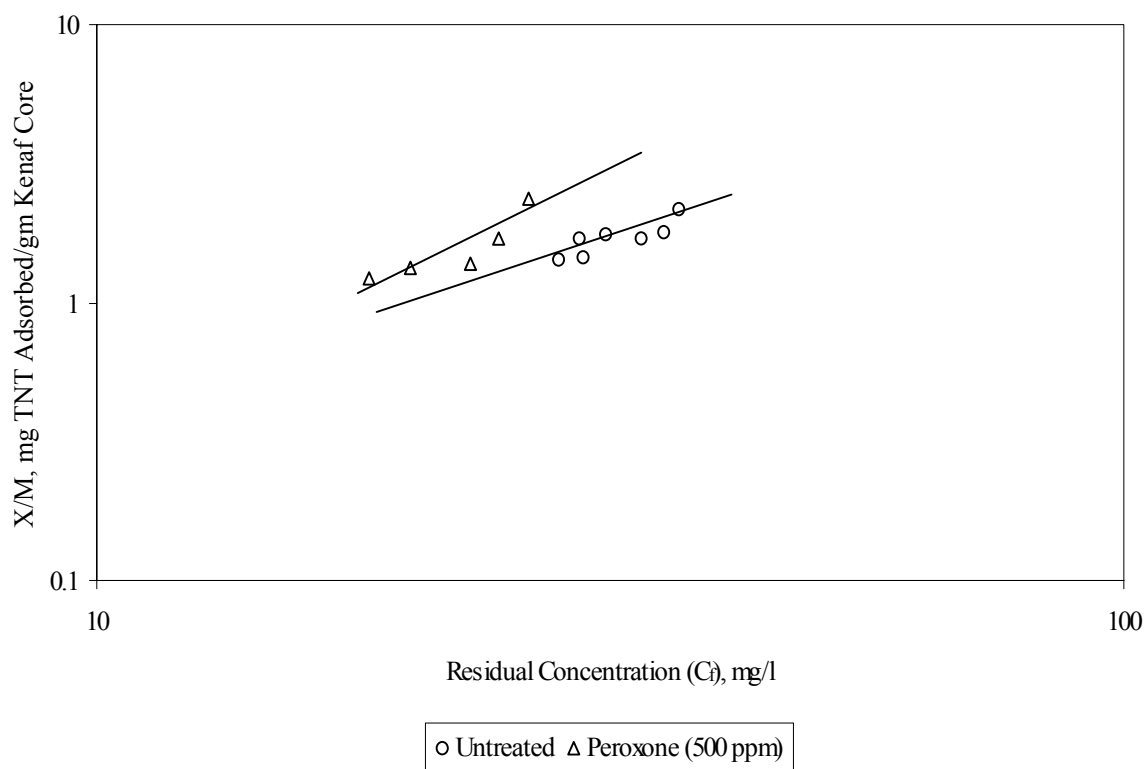
Figure C.21. Effect of peroxone pretreatment of kenaf core on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
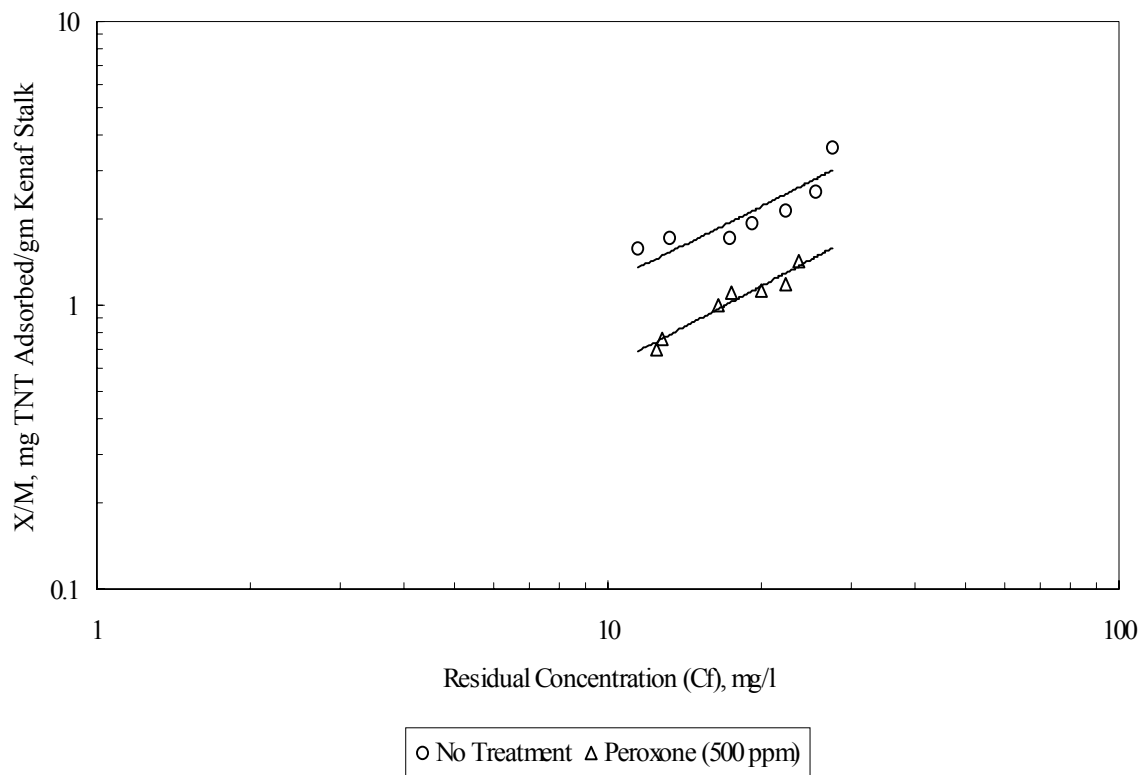
Figure C.22. Effect of peroxone pretreatment of kenaf stalk on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
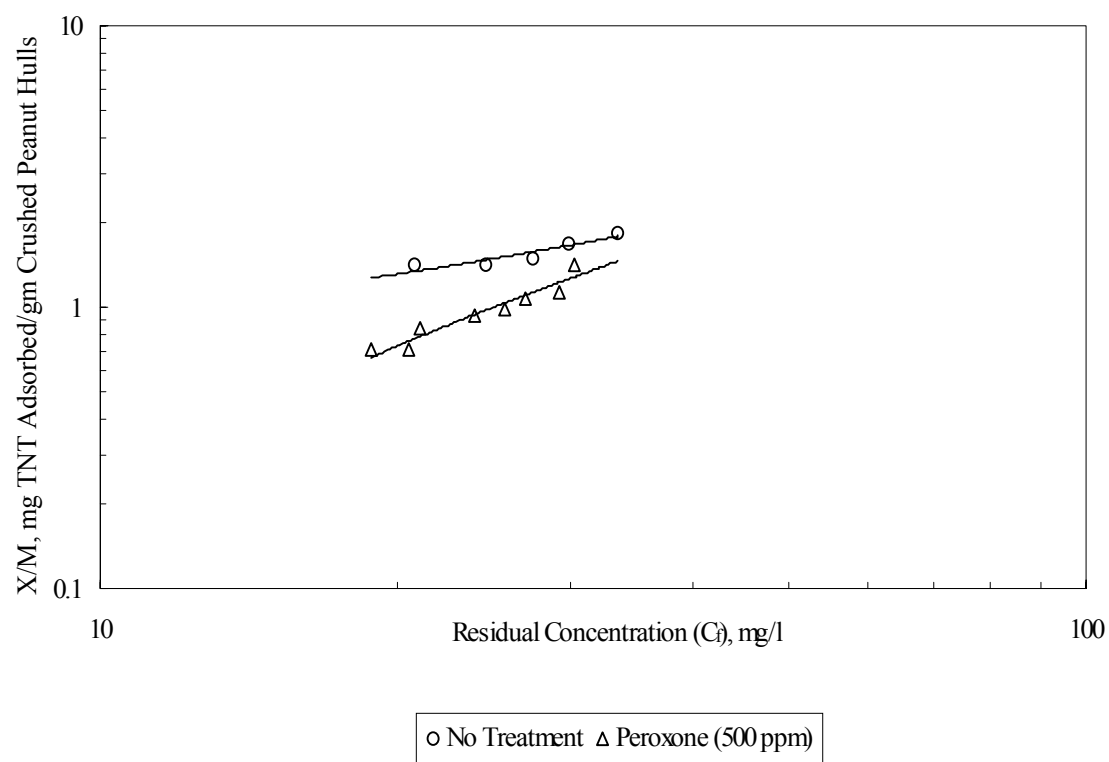
Figure C.23. Effect of peroxone pretreatment of crushed peanut hulls on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
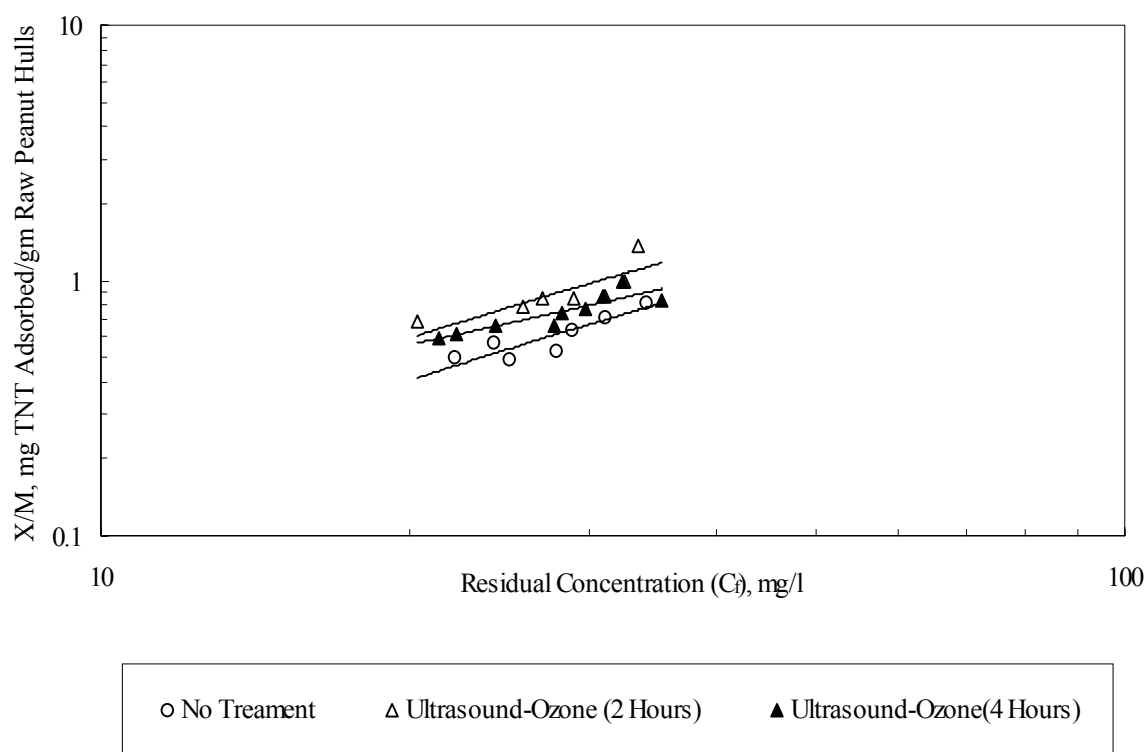
Figure C.24. Effect of ultrasound pretreatment of raw peanut hulls on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
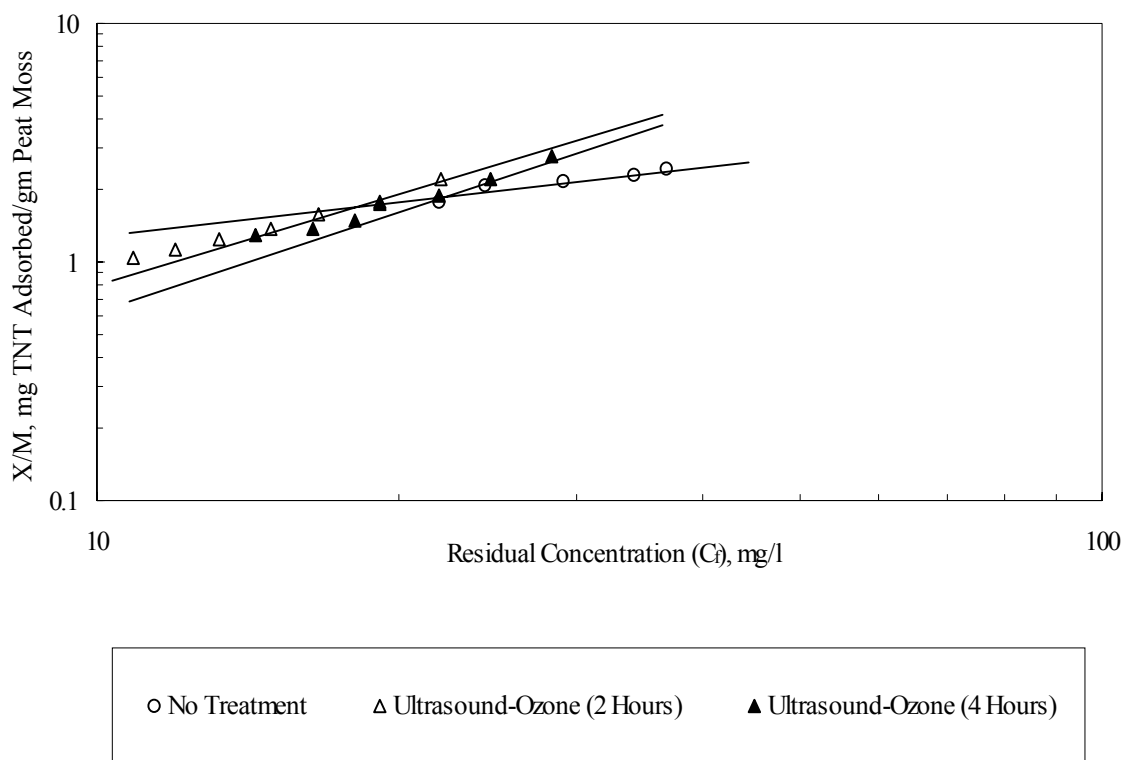
Figure C.25. Effect of ultrasound pretreatment of peat moss on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
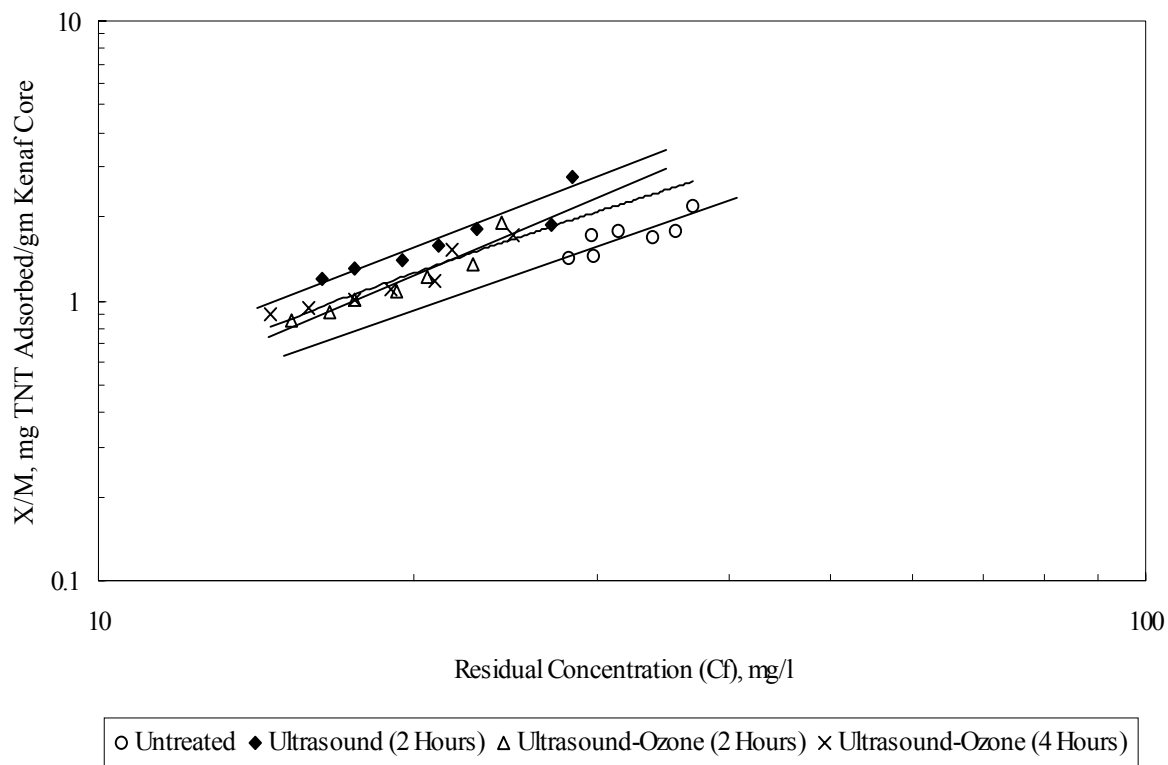
Figure C.26. Effect of ultrasound pretreatment of kenaf core on the adsorption of TNT (Temperature = 25 $^0$ C, pH = 5).
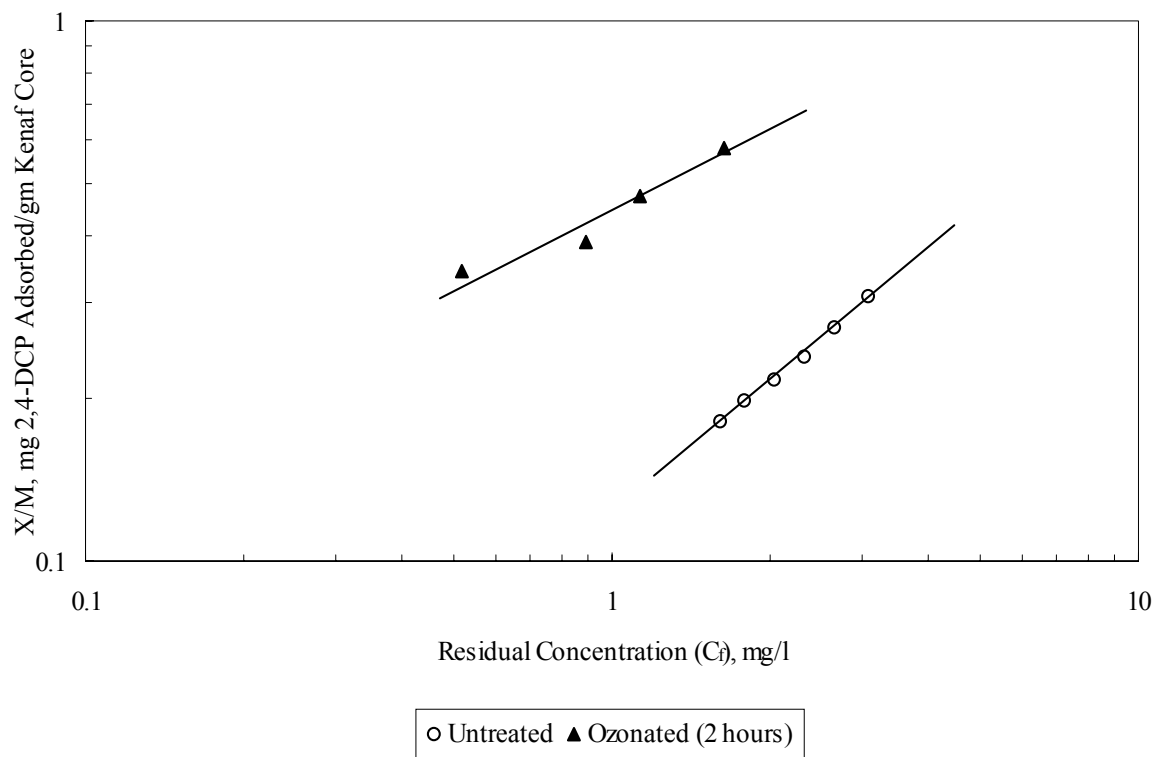
Figure C.27. Effect of pretreatment of kenaf core with ozone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
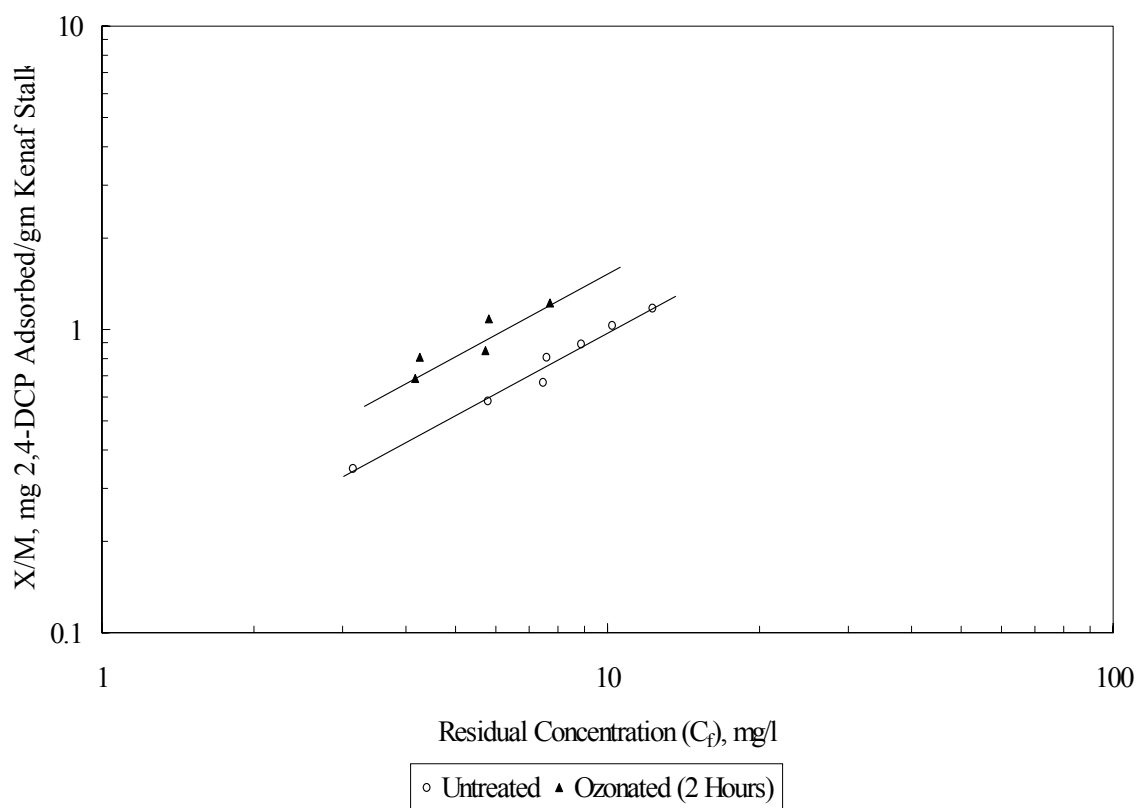
Figure C.28. Effect of pretreatment of kenaf stalk with ozone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
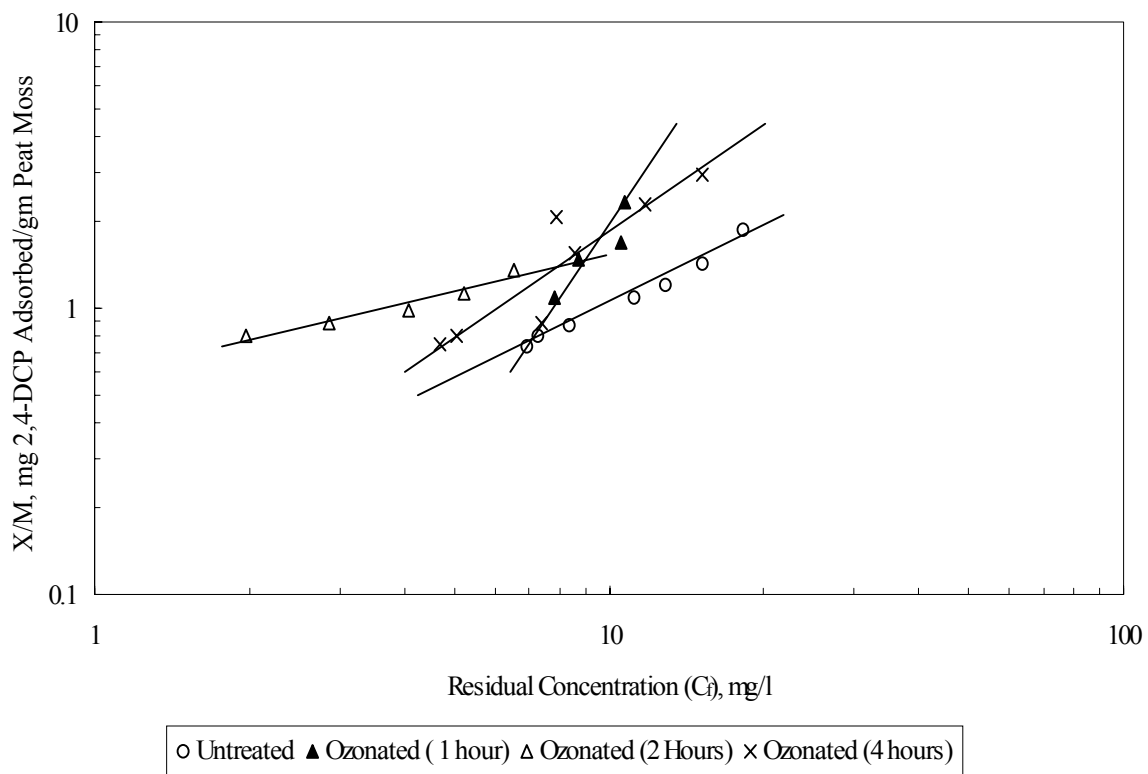
Figure C.29. Effect of pretreatment of peat moss with ozone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
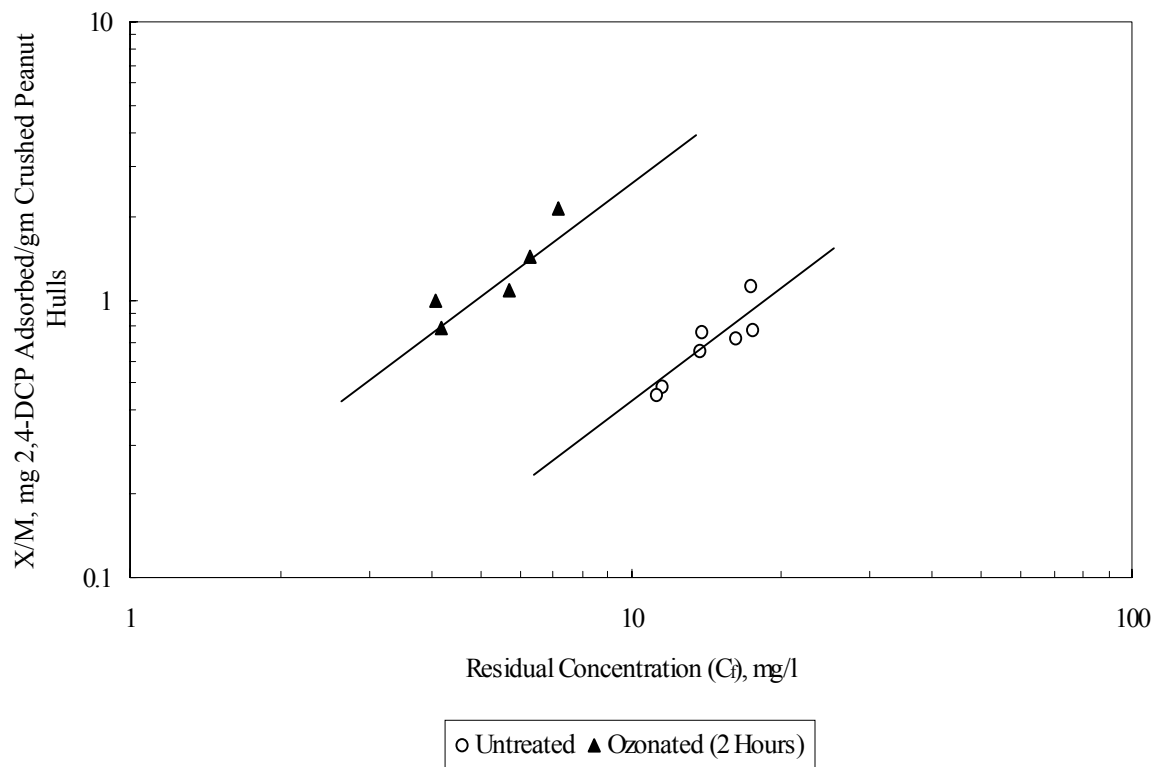
Figure C.30. Effect of pretreatment of crushed peanut hulls with ozone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
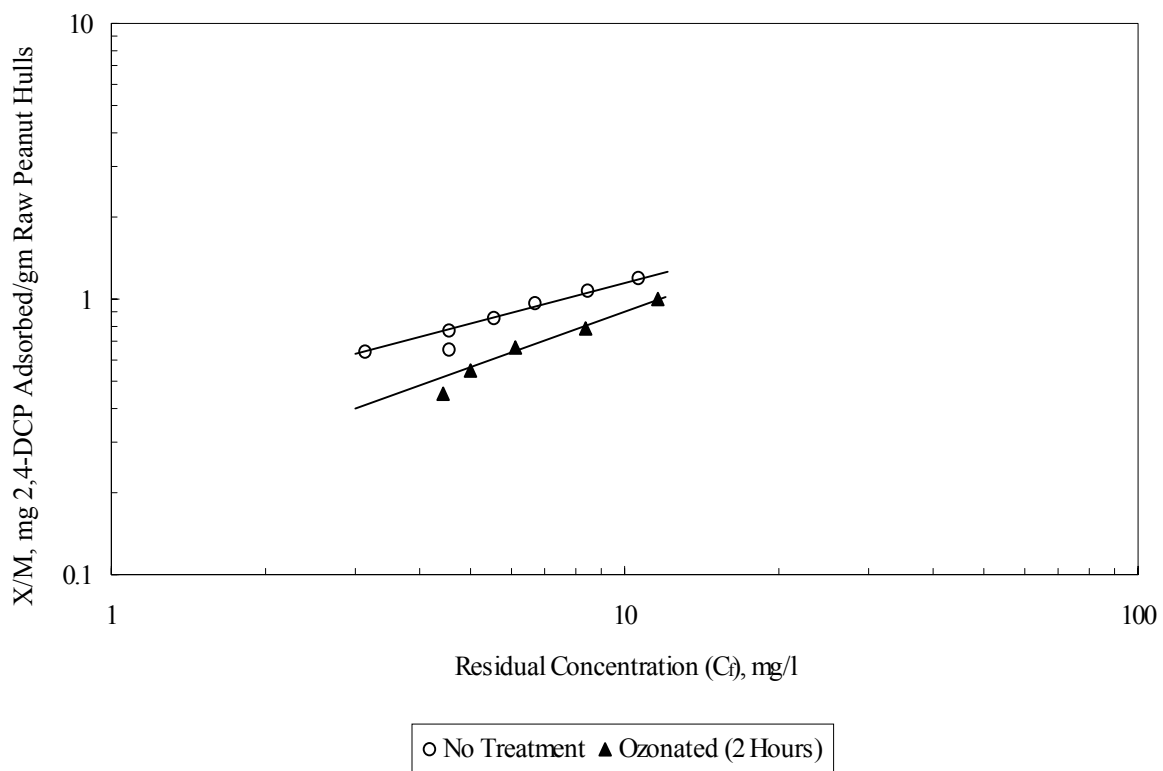
Figure C.31. Effect of pretreatment of raw peanut hulls with ozone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
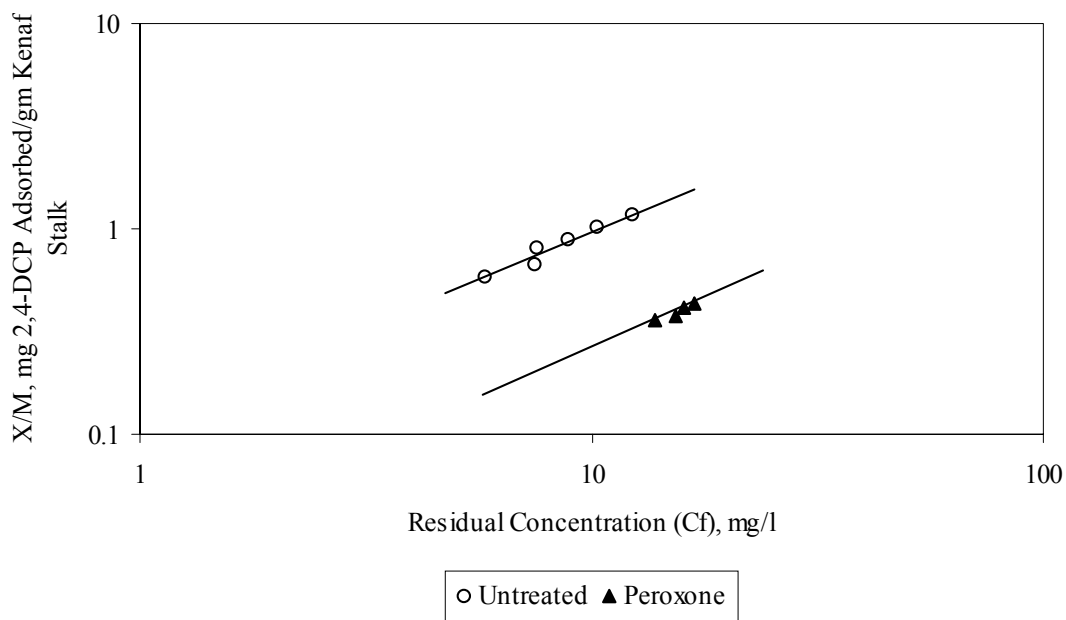
Figure C.32. Effect of pretreatment of kenaf stalk with peroxone on the adsorption of 2,4-DCP (Temperature = 25 $^0$ C, pH = 5).
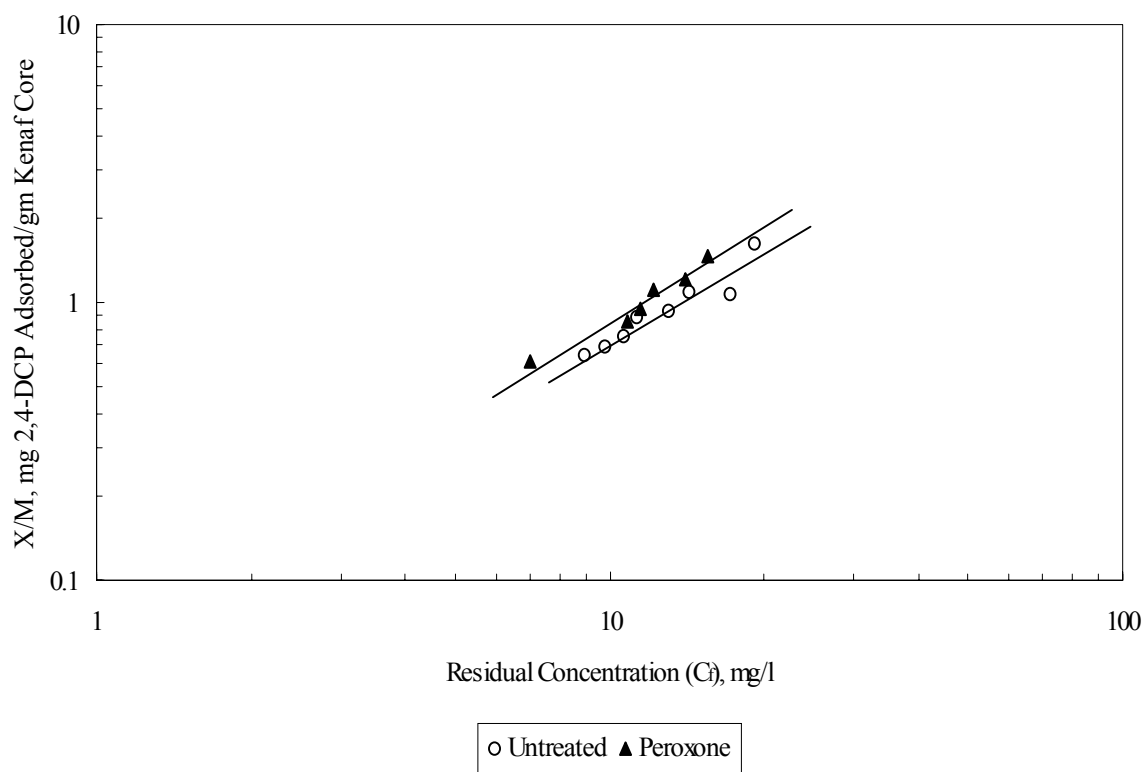
Figure C.33. Effect of pretreatment of kenaf core with peroxone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
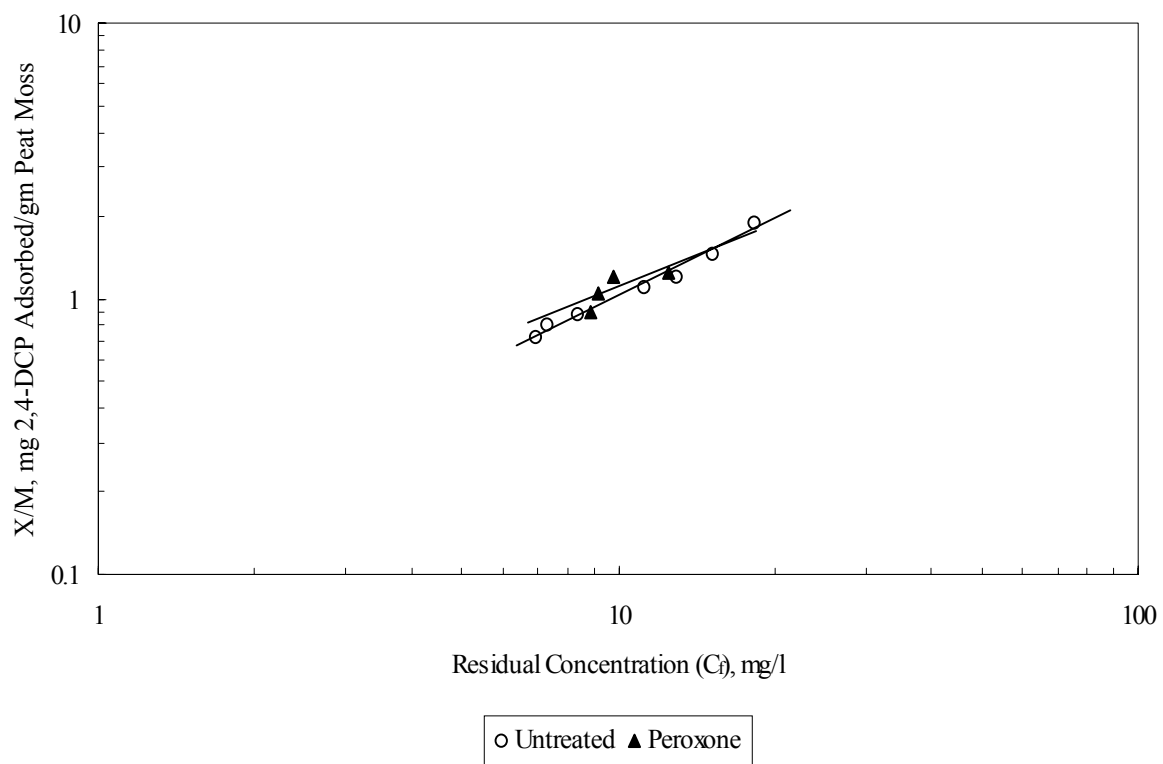
Figure C.34. Effect of pretreatment of peat moss with peroxone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
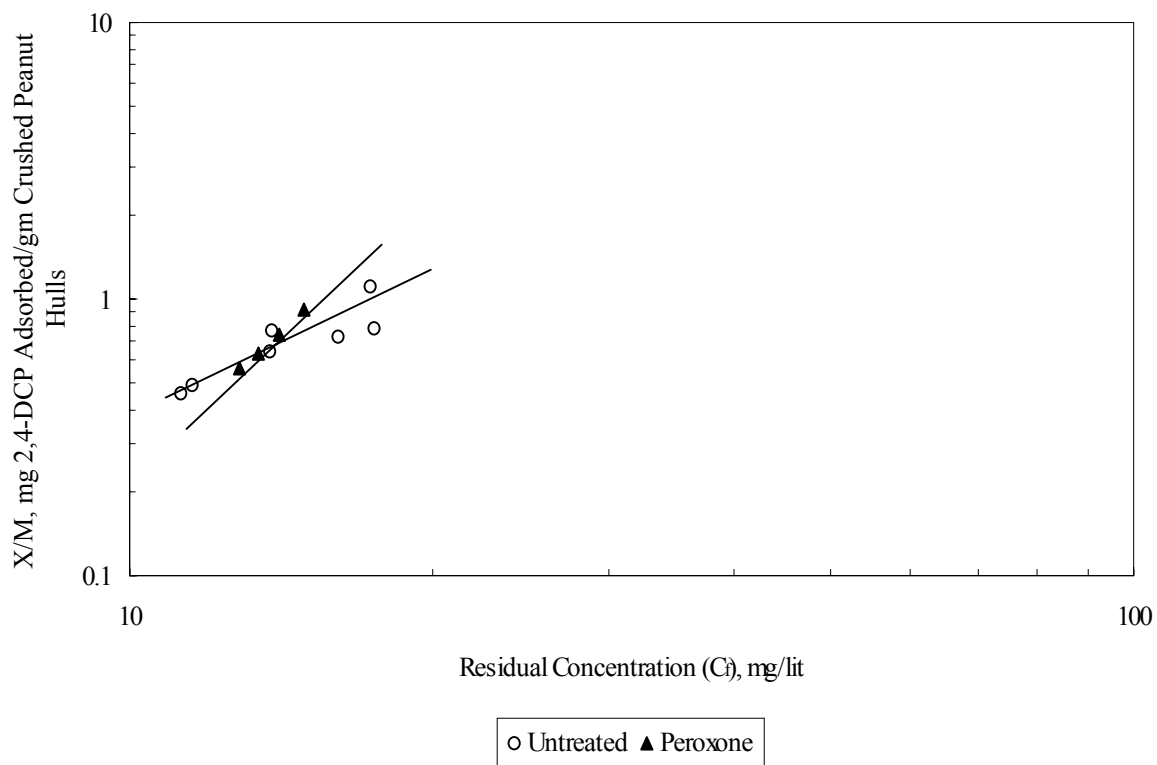
Figure C.35. Effect of pretreatment of crushed peanut hulls with peroxone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).

Figure C.36. Effect of pretreatment of raw peanut hulls with peroxone on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
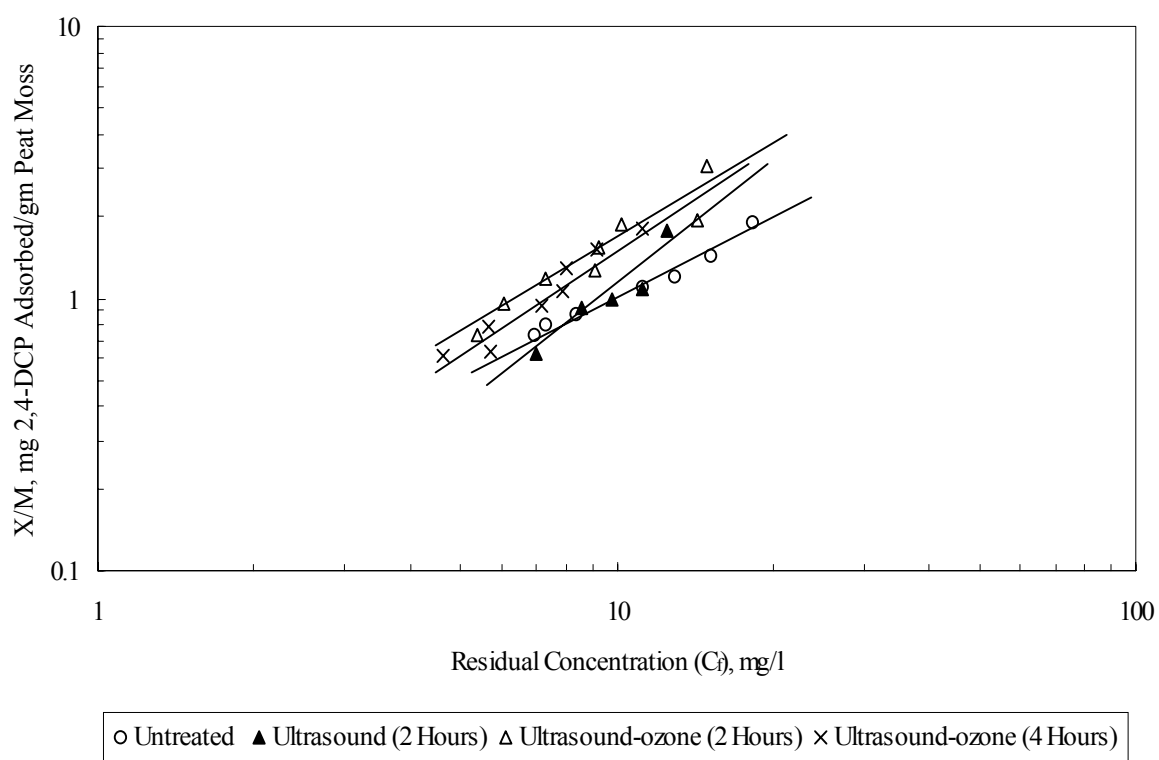
Figure C.37. Effect of pretreatment of peat moss with ultrasound on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
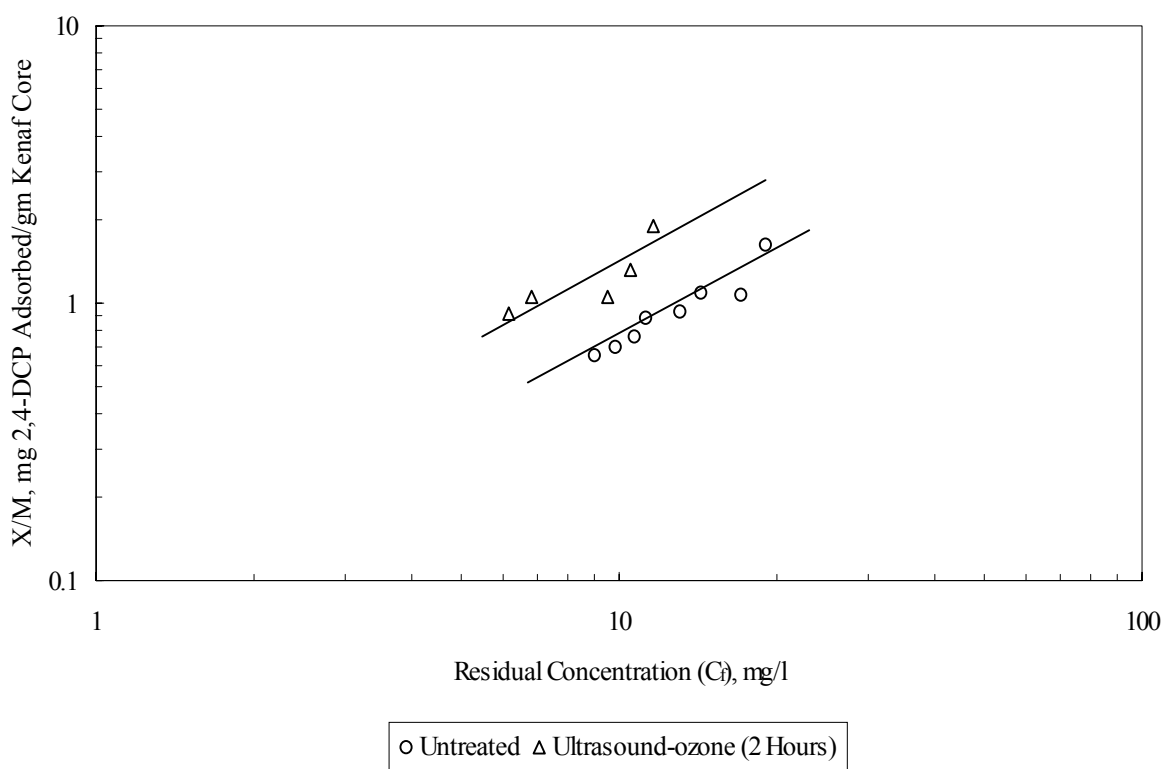
Figure C.38. Effect of pretreatment of kenaf core with ultrasound on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
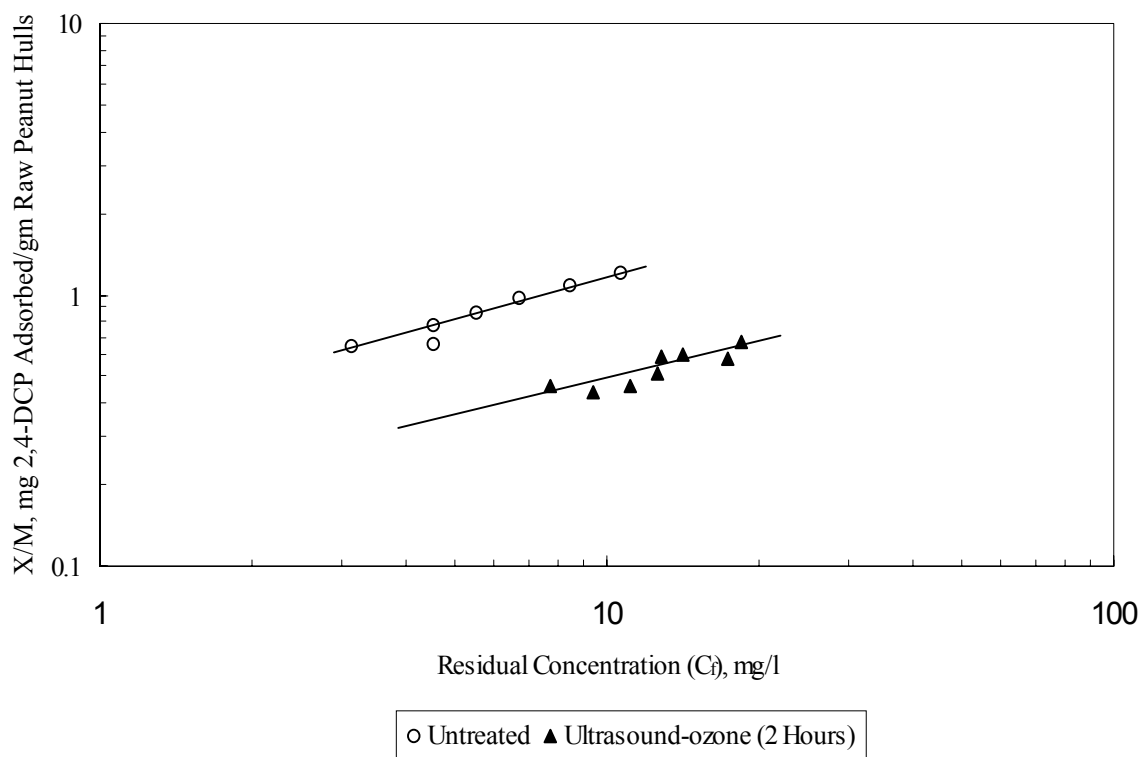
Figure C.39. Effect of pretreatment of raw peanut hulls with ultrasound on the adsorption of 2,4-DCP (Temperature = 25 $^0$C, pH = 5).
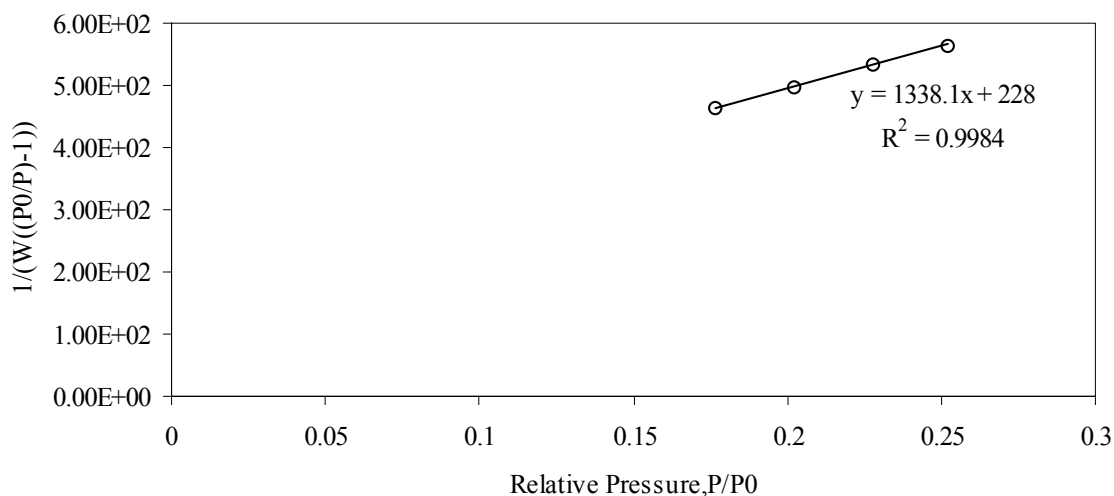
Figure C.40.  BET plot for surface area analysis of kenaf core (Run 1).

BET Equation : $1 / [W((P0/P)-1)] = 1 / W_mC + (C-1)(P/P0) / W_mC$

where,

W = weight of gas adsorbed at relative pressure, g

P0 = saturated pressure of gas adsorbate, mm Hg

P = actual gas pressure, mm Hg

Wm = mololayer weight of gas adsorbed, g

C = constant, energy of adsorption in monolayer

Note: Sample weight = 0.4471 g

P/P0 Tolerance = 0

Equilibration Time = 15 minutes

Analysis Time = 79 minutes

Gas type = Nitrogen

Cross-sectional area of adsorbate = 16.2 $(A^0)^2$/molecule

Molecular weight of adsorbate gas = 28.0134 g/mole

Ambient temperature = 292.118 K

Bath temperature = 77.350 K

Saturated pressure of nitrogen, P0 = 764.63 mm Hg

Out gas temperature = 23 $^0$ C

Out gas time = 20.0 hours

BET constant, C = 6.808

Surface area of kenaf core = 2.231 $m^2$/g
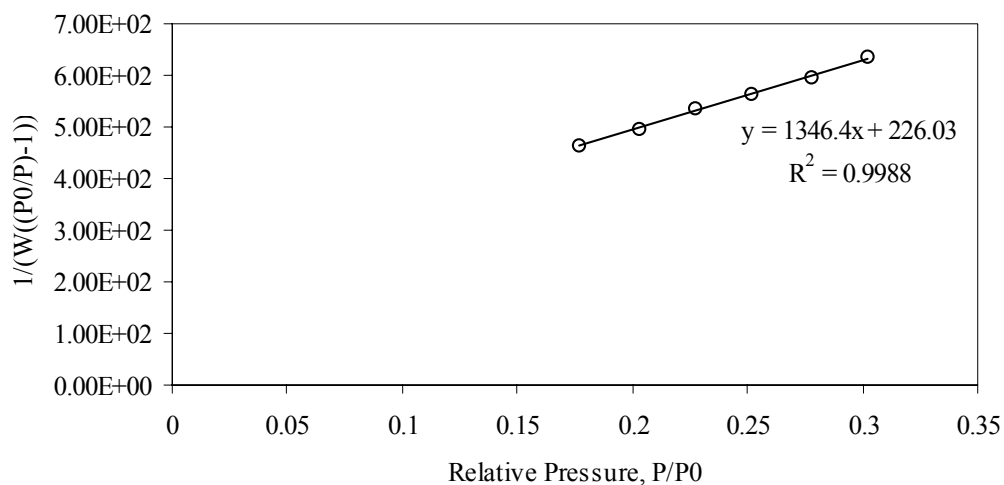
Figure 41.  BET plot for surface area analysis of kenaf core (Run 2)

Note: Sample weight = 0.4471 g
P/P0 Tolerance = 0
Equilibration Time = 15 minutes
Analysis Time = 79 minutes
Gas type = Nitrogen
Cross-sectional area of adsorbate = 16.2 $(A^0)^2$/molecule
Molecular weight of adsorbate gas = 28.0134 g/mole
Ambient temperature = 292.118 K
Bath temperature = 77.350 K
Saturated pressure of nitrogen, P0 = 764.63 mm Hg
Out gas temperature = 23 $^0$ C
Out gas time = 20.0 hours
BET constant, C = 6.949
Surface area of kenaf core = 2.215 $m^2$/g

APPENDIX D

DYNAMIC COLUMN STUDIES DATA

Table D.1. Breakthrough curve data for kenaf core using 2,4-DCP. EBCT = 20 minutes.

| Time, hours | Effluent Concentration, mg/l |
|---|---|
| 0 | 0 |
| 0.5 | 0 |
| 1 | 11.654 |
| 2 | 26.688 |
| 5.5 | 69.857 |
| 6.5 | 68.97 |
| 17 | 81.242 |
| 21.5 | 71.135 |
| 23 | 72.763 |
| 29 | 78.008 |
| 41 | 81.115 |
| 47 | 83.353 |

Table D.2. Breakthrough curve data for kenaf core using 2,4-DCP. EBCT = 60 minutes.

| Time, hours | Effluent Concentration, mg/l |
|---|---|
| 0 | 0 |
| 0.5 | 0 |
| 1 | 0 |
| 2 | 1.134 |
| 5.5 | 33.438 |
| 6.5 | 45.675 |
| 17 | 70.841 |
| 21.5 | 69.934 |
| 23 | 70.818 |
| 29 | 80.449 |
| 41 | 81.390 |
| 47 | 75.607 |

Note : Initial 2,4- DCP concentration = 83.54 mg/l
Mass of kenaf core in column ($M_c$) = 56 gm

Table D.3. Breakthrough curve data for kenaf stalk using 2,4-DCP. EBCT = 20 minutes.

| Time, hours | Effluent Concentration, mg/l |
| --- | --- |
| 0 | 0 |
| 0.5 | 28.574 |
| 1 | 47.216 |
| 4 | 64.518 |
| 6 | 68.656 |
| 14 | 65.067 |
| 21.5 | 70.702 |
| 40 | 74.138 |

Table D.4. Breakthrough curve data for kenaf stalk using 2,4-DCP. EBCT = 60 minutes.

| Time, hours | Effluent Concentration, mg/l |
| --- | --- |
| 0 | 0 |
| 1 | 20.657 |
| 4 | 39.752 |
| 6 | 50.863 |
| 14 | 58.434 |
| 21.5 | 66.311 |
| 40 | 68.394 |

Note : Initial 2,4-DCP concentration = 75.2 mg/l
    Mass of kenaf stalk in column ($M_c$) = 47 gm

Table D.5. Breakthrough curve data for raw peanut hulls using 2,4-DCP. EBCT = 20 minutes.

| Time, hours | Effluent Concentration, mg/l |
| --- | --- |
| 0 | 0 |
| 1 | 32.518 |
| 3 | 48.791 |
| 16 | 64.843 |
| 21 | 62.396 |
| 25 | 67.478 |
| 42 | 69.478 |

Table D.6. Breakthrough curve data for raw peanut hulls using 2,4-DCP. EBCT = 60 minutes.

| Time, hours | Effluent Concentration, mg/l |
| --- | --- |
| 0 | 0 |
| 1 | 20.657 |
| 3 | 32.980 |
| 16 | 52.461 |
| 21 | 59.071 |
| 25 | 59.704 |
| 42 | 59.325 |

Note: Initial 2,4-DCP concentration = 67.18 mg/l.
    Mass of raw peanut hulls in column ($M_c$) = 118 gm

APPENDIX E

BREAKTHROUGH CURVES
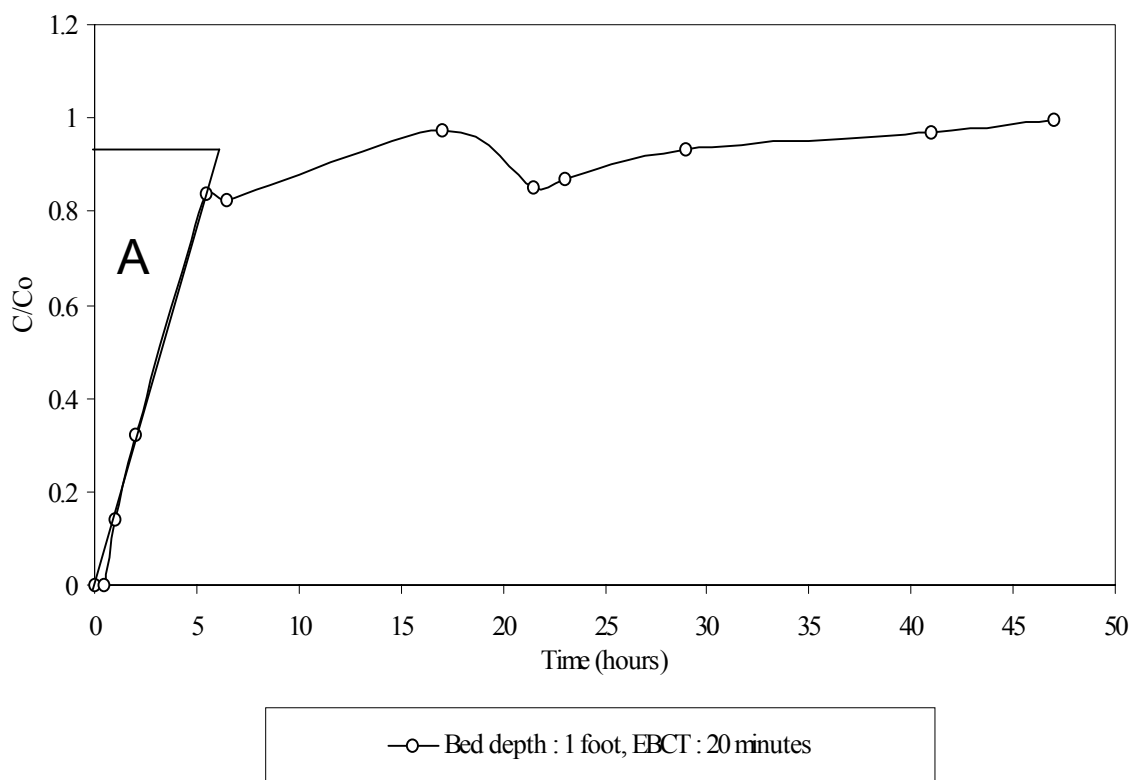
Figure E.1. Breakthrough curve for kenaf core with 20 minutes EBCT.
A: Amount of adsorbate removed = Area of triangle x Flowrate
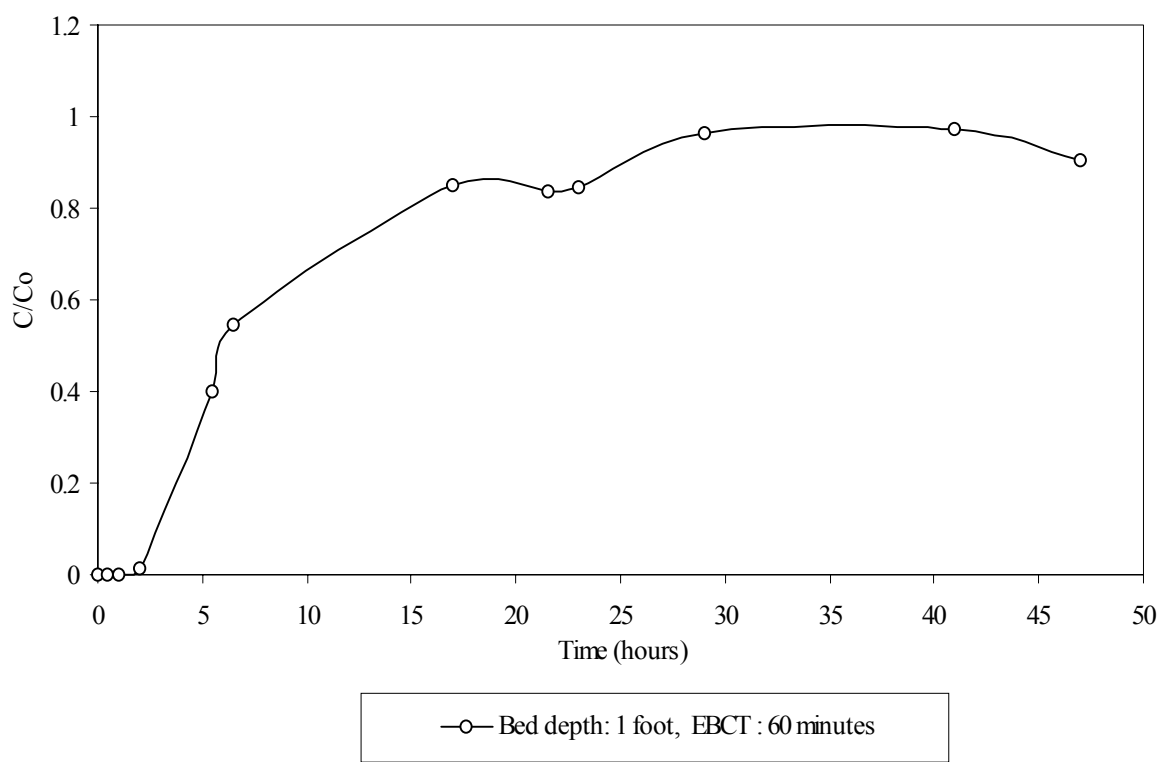
Figure E.2. Breakthrough curve for kenaf core with 60 minutes EBCT.
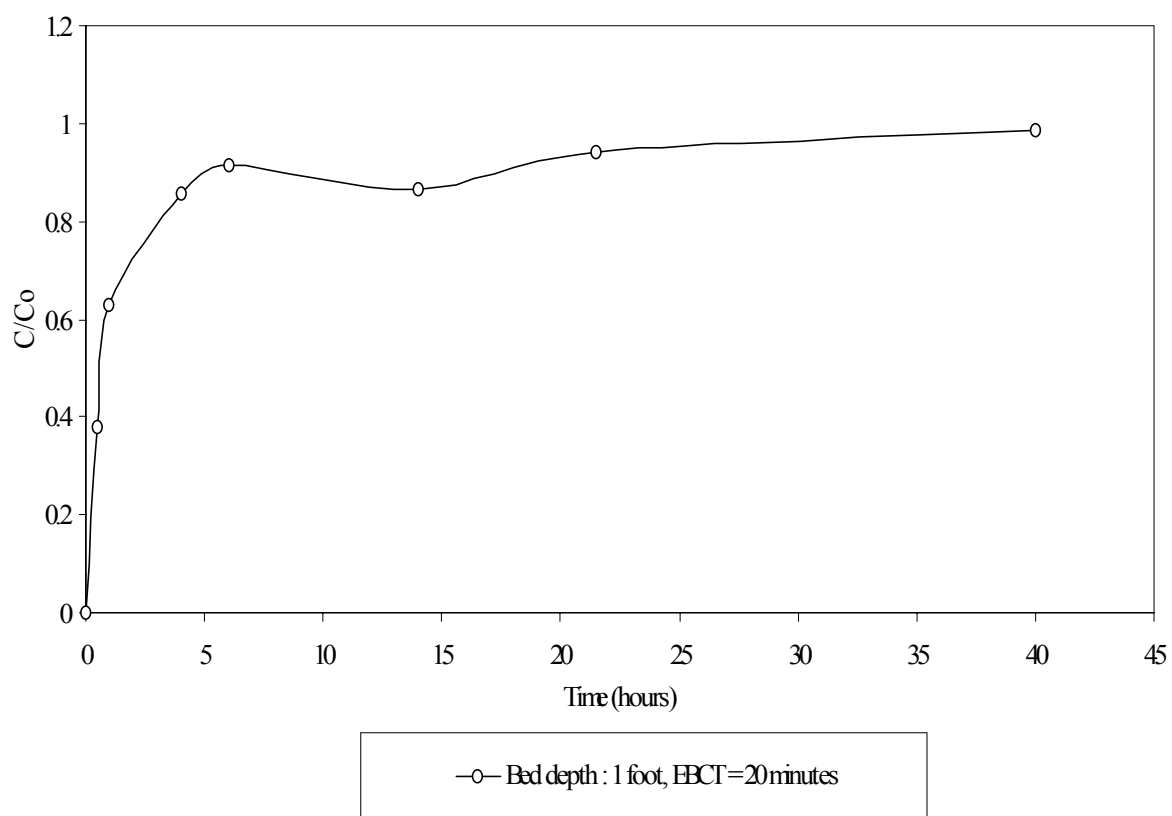
Figure E.3. Breakthrough curve for kenaf stalk with 20 minutes EBCT.
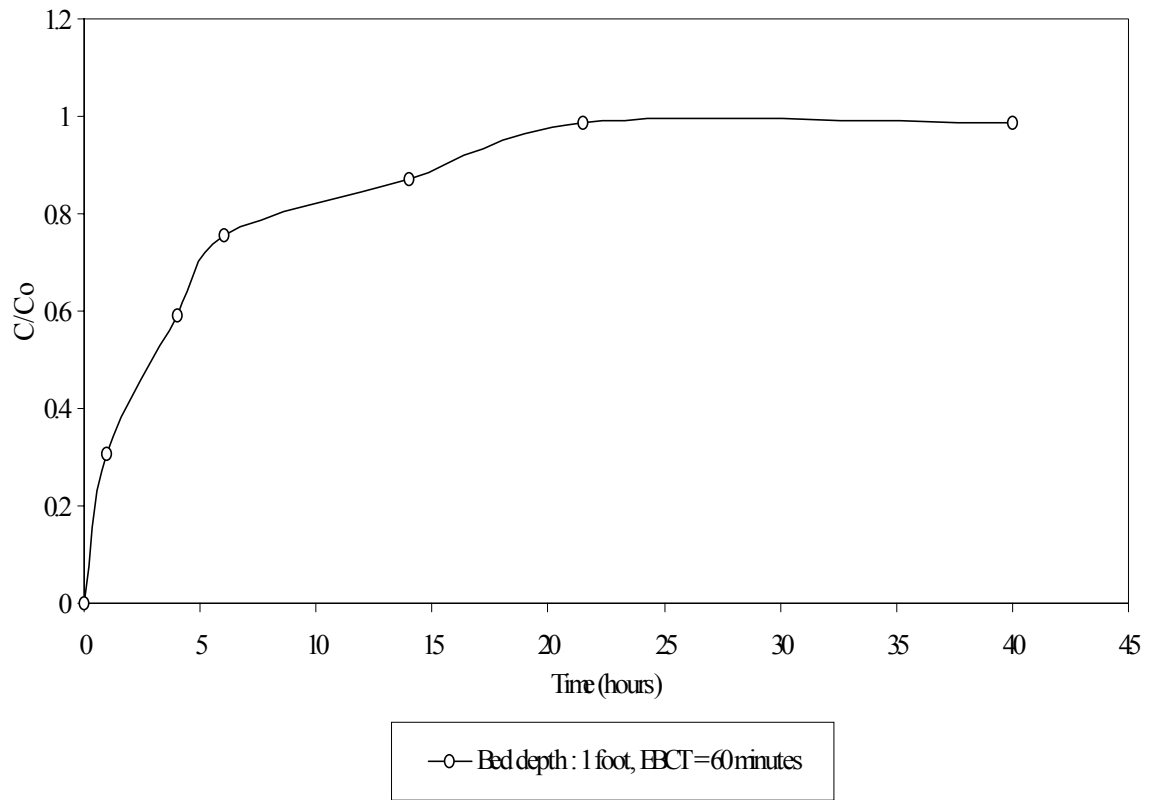
Figure E.4. Breakthrough curve for kenaf stalk with 60 minutes EBCT.
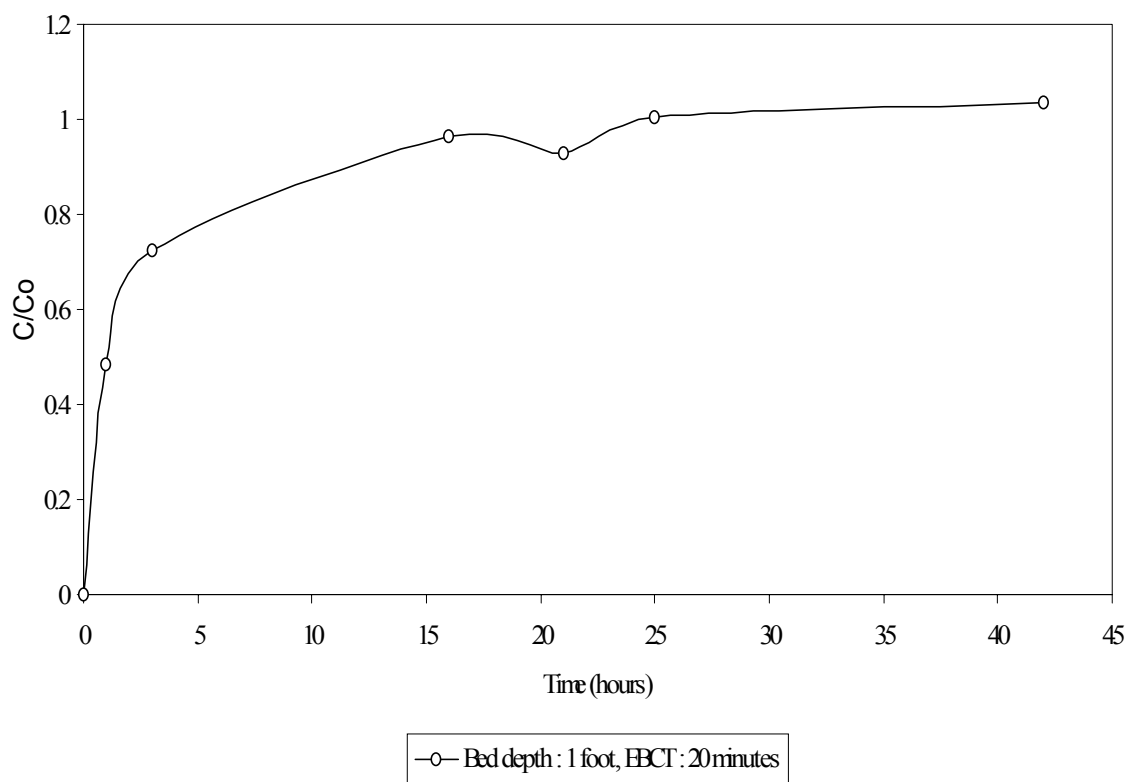
Figure E.5. Breakthrough curve for raw peanut hulls with 20 minutes EBCT.
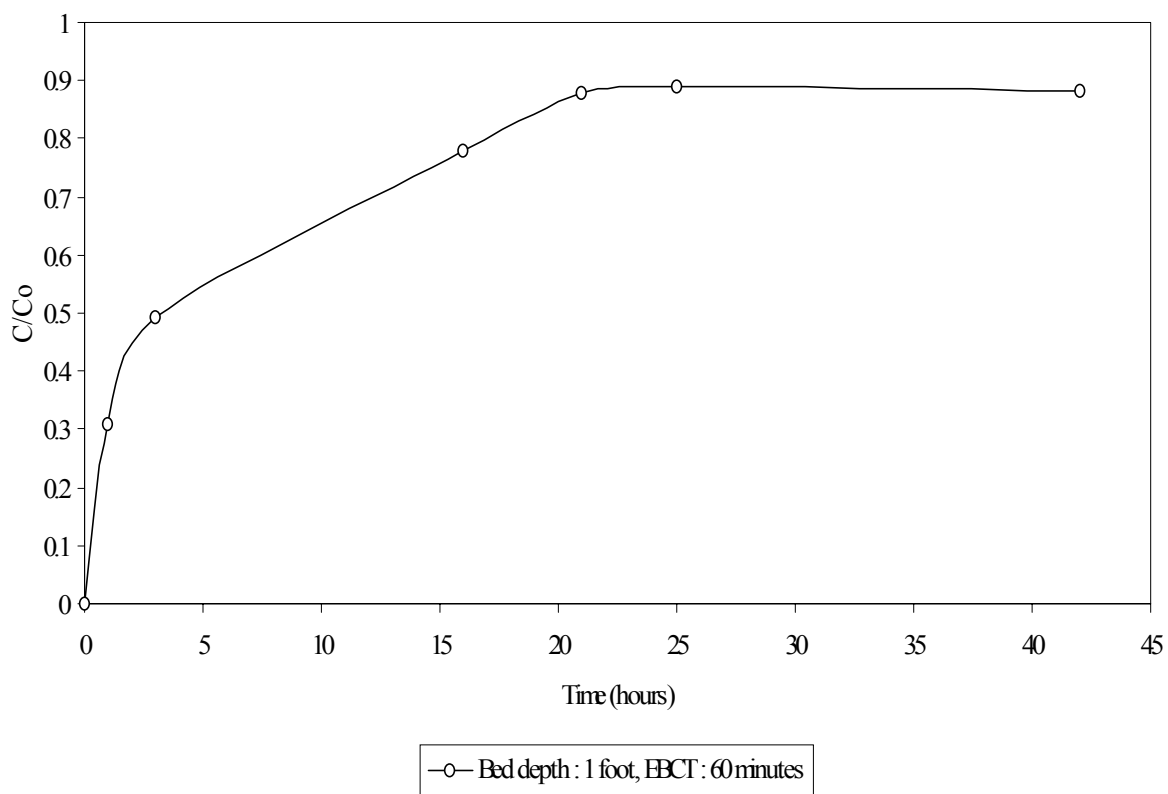
Figure E.6. Breakthrough curve for raw peanut hulls with 60 minutes EBCT.

APPENDIX F

SEM MICROGRAPHS
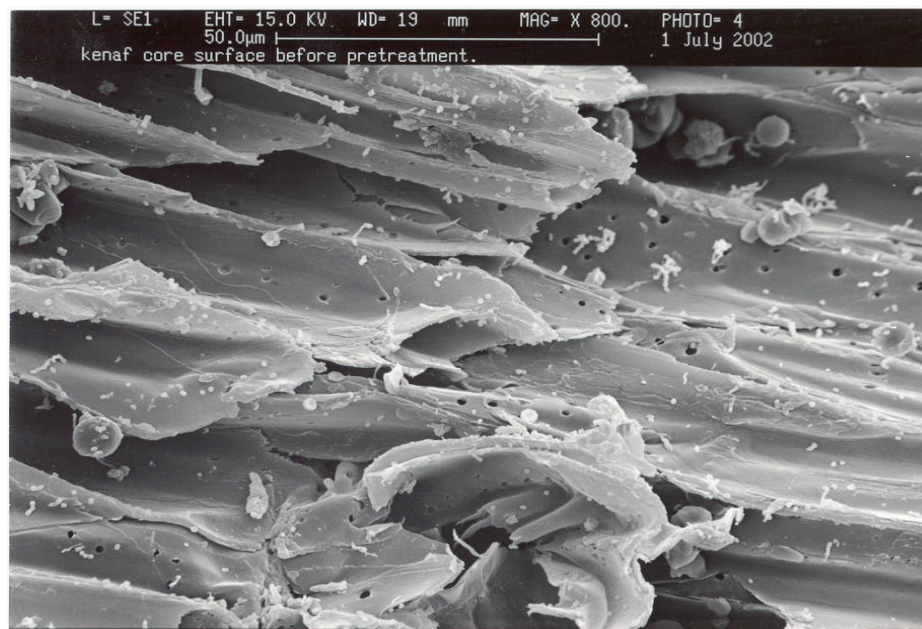
Figure F.1. SEM micrograph of kenaf core. Magnification : 1 x 800.
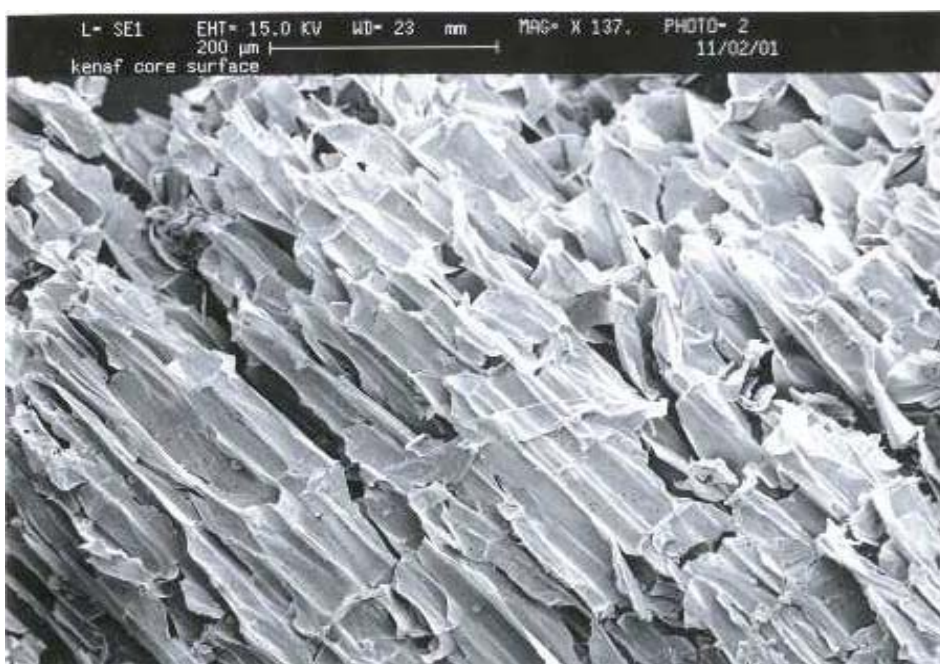
Figure F.2. SEM micrograph of kenaf core after ozone pretreatment.
Magnification : 1 x 137.
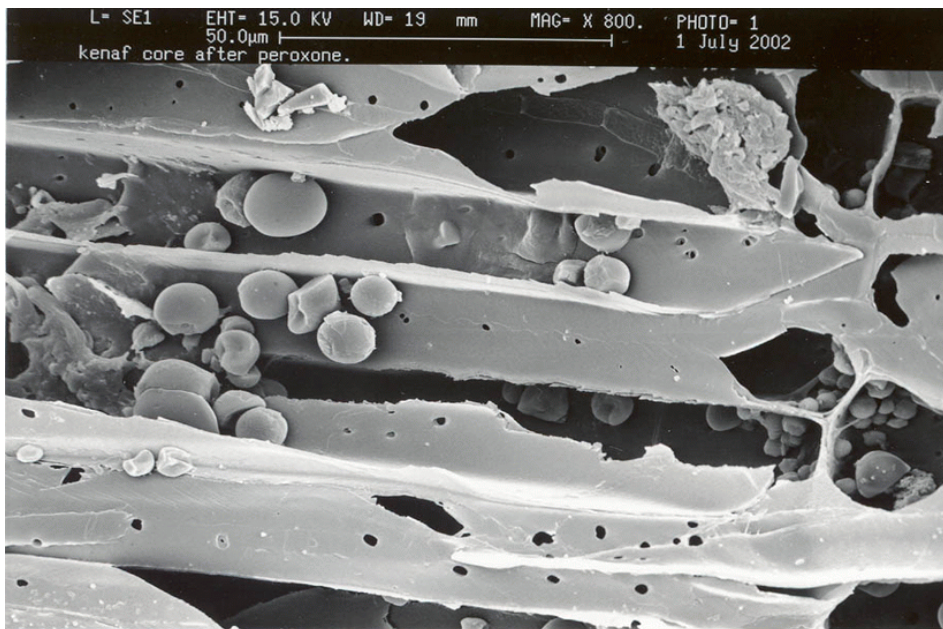
Figure F.3. SEM micrograph of kenaf core after peroxone pretreatment.
Magnification: 1 x 800.
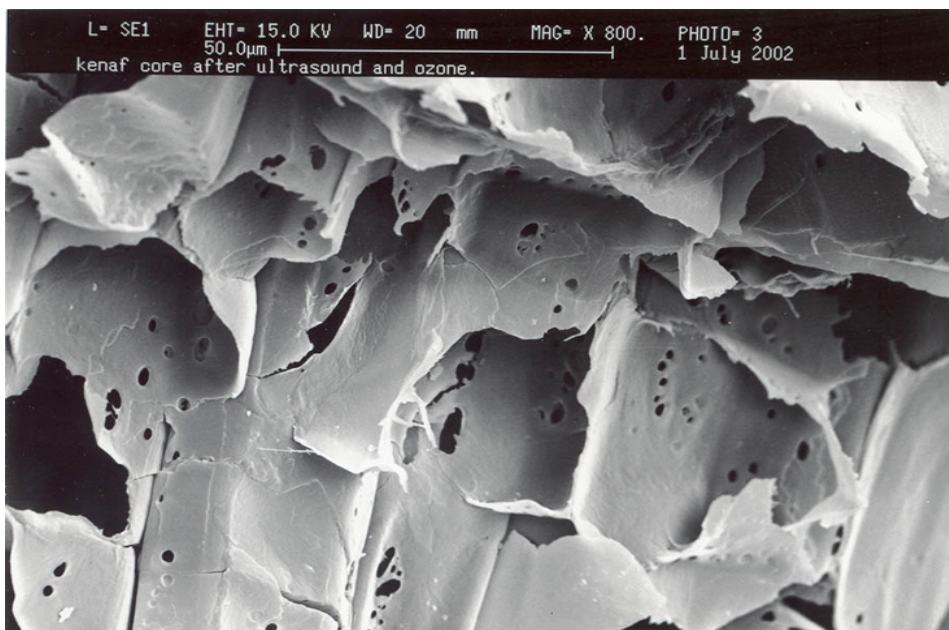


Figure F.4. SEM micrograph of kenaf core after combination of
ultrasound and ozone pretreatment. Magnification; 1 x 800.
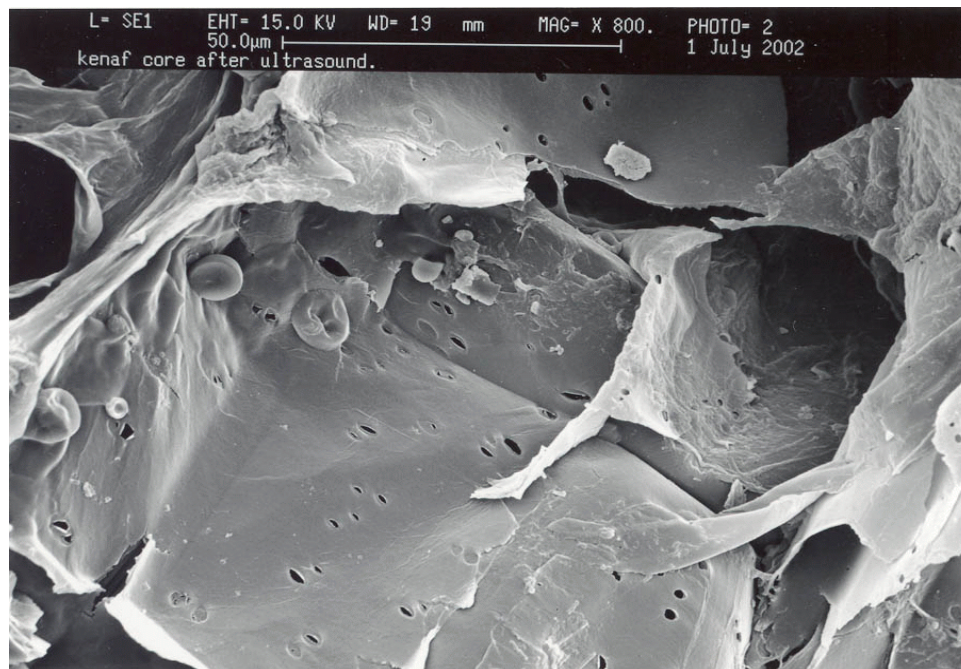
Figure F.5. SEM micrograph of kenaf core after ultrasound pretreatment. Magnification: 1 x 800.
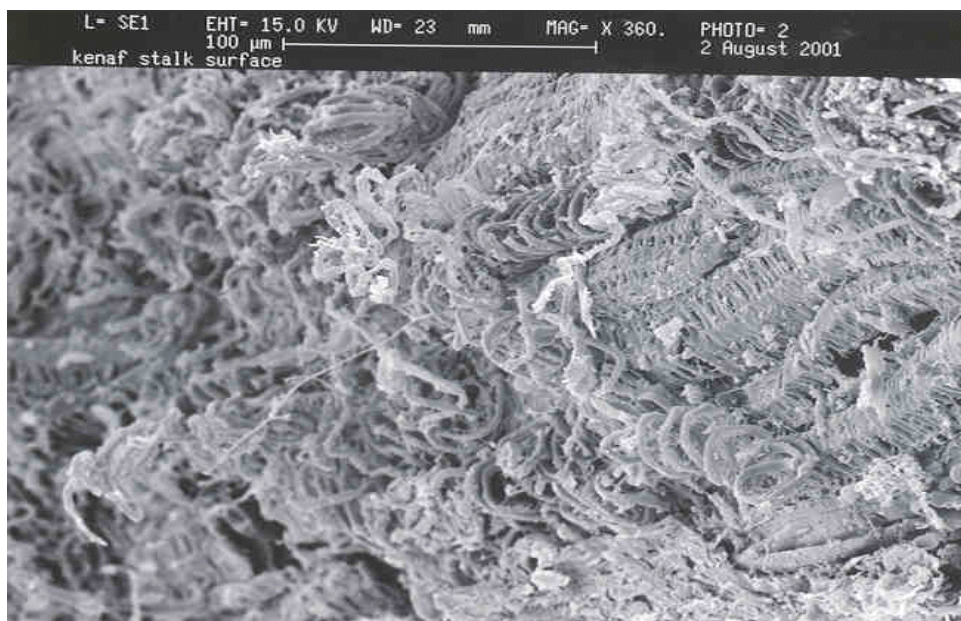


Figure F.6. SEM micrograph of kenaf stalk. Magnification: 1 x 360.
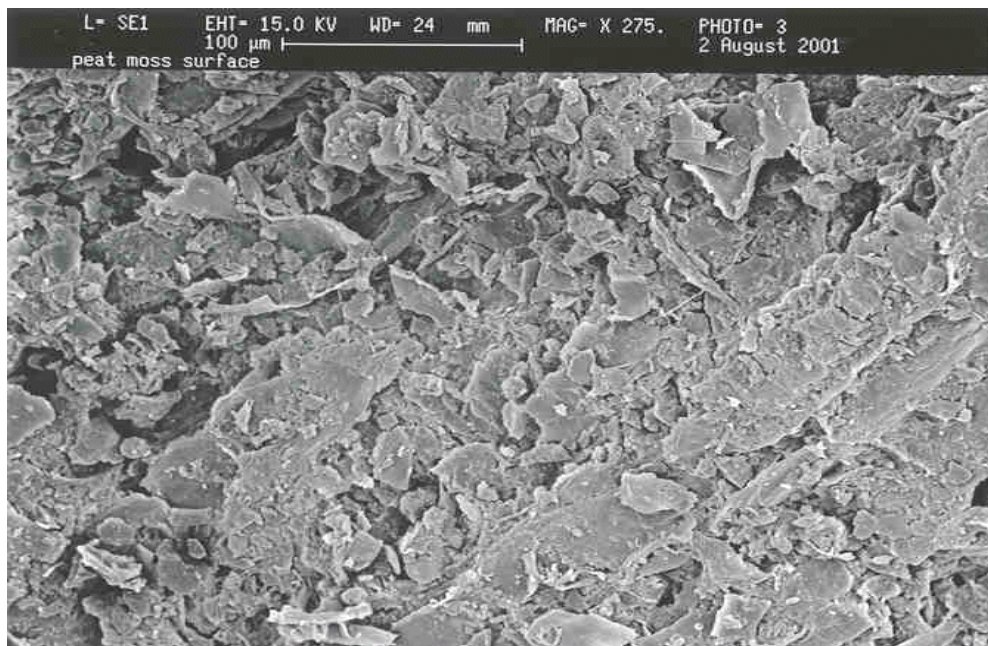
Figure F.7. SEM micrograph of peat moss. Magnification: 1 x 275
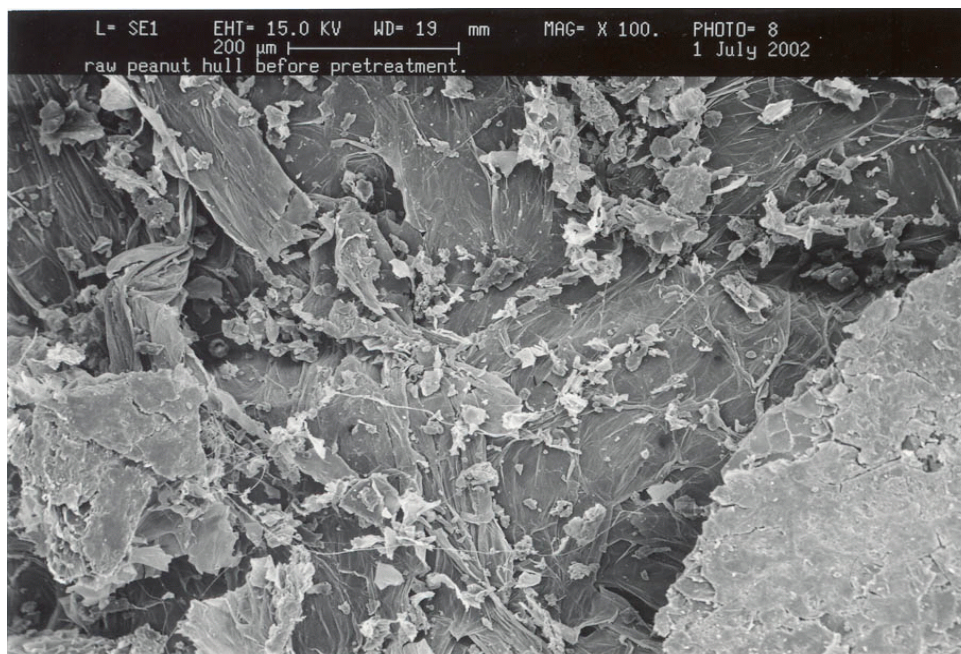


Figure F.8. SEM micrograph of raw peanut hulls. Magnification: 1 x 100.
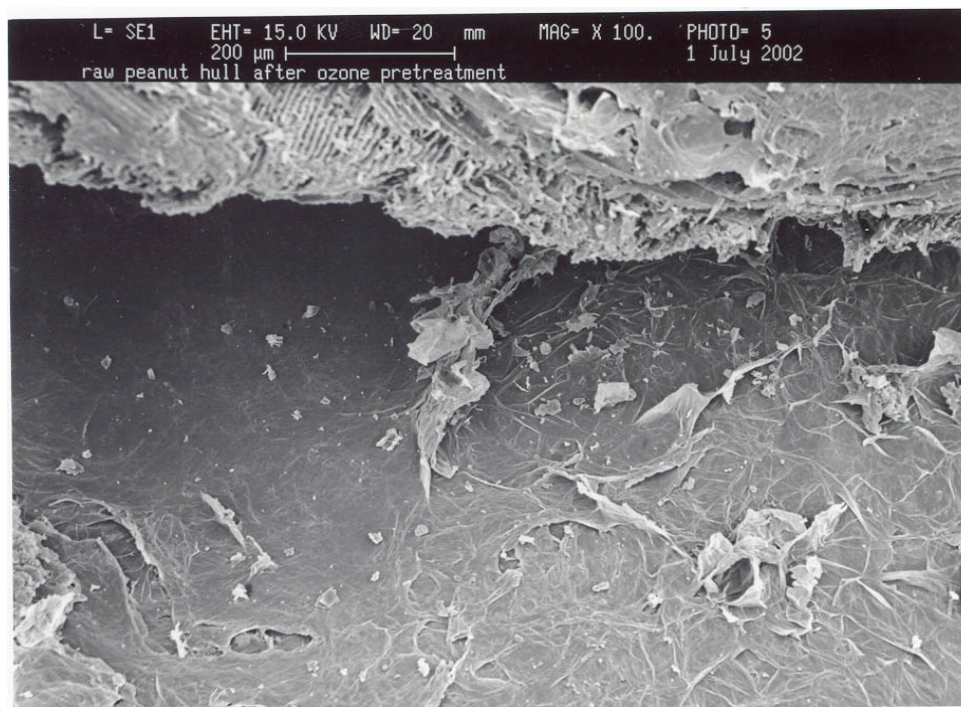
Figure F.9. SEM micrograph of raw peanut hulls after ozone pretreatment. Magnification: 1 x 100.
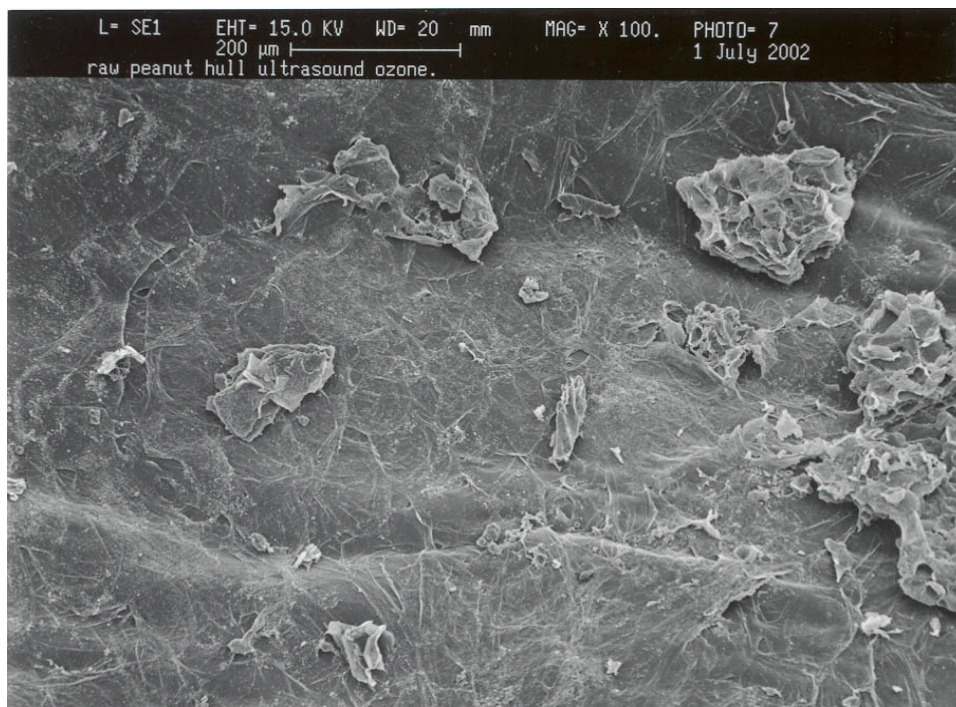


Figure F.10. SEM micrograph of raw peanut hulls after combination of ultrasound and ozone pretreatment. Magnification: 1 x 100.
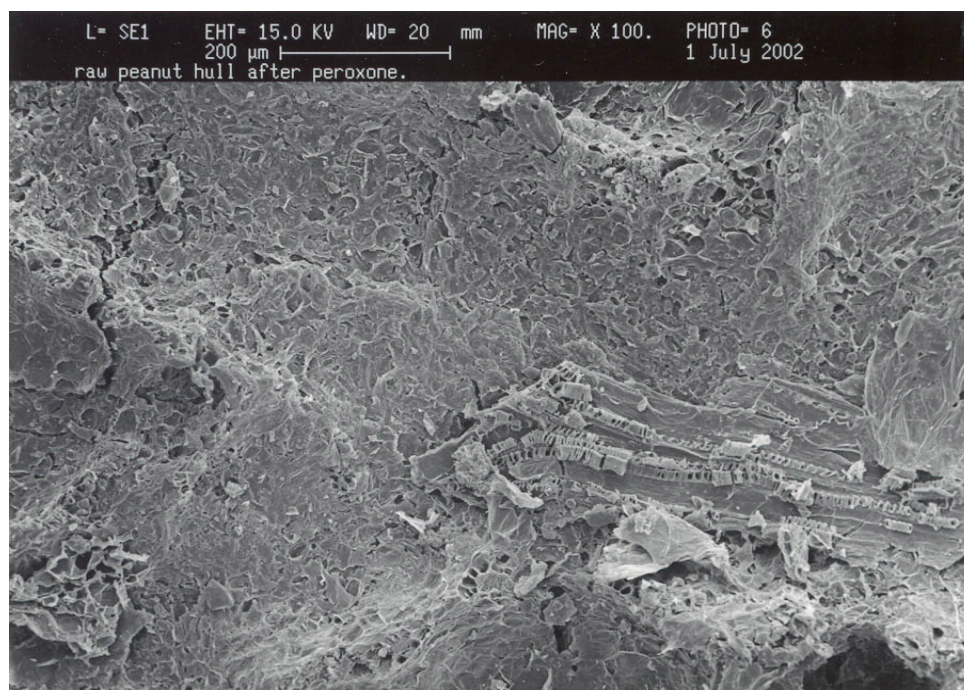
Figure F.11. SEM micrograph of raw peanut hulls after peroxone pretreatment. Magnification: 1 x 100.



Figure F.12. SEM micrograph of crushed peanut hulls. Magnification: 1 x 400.
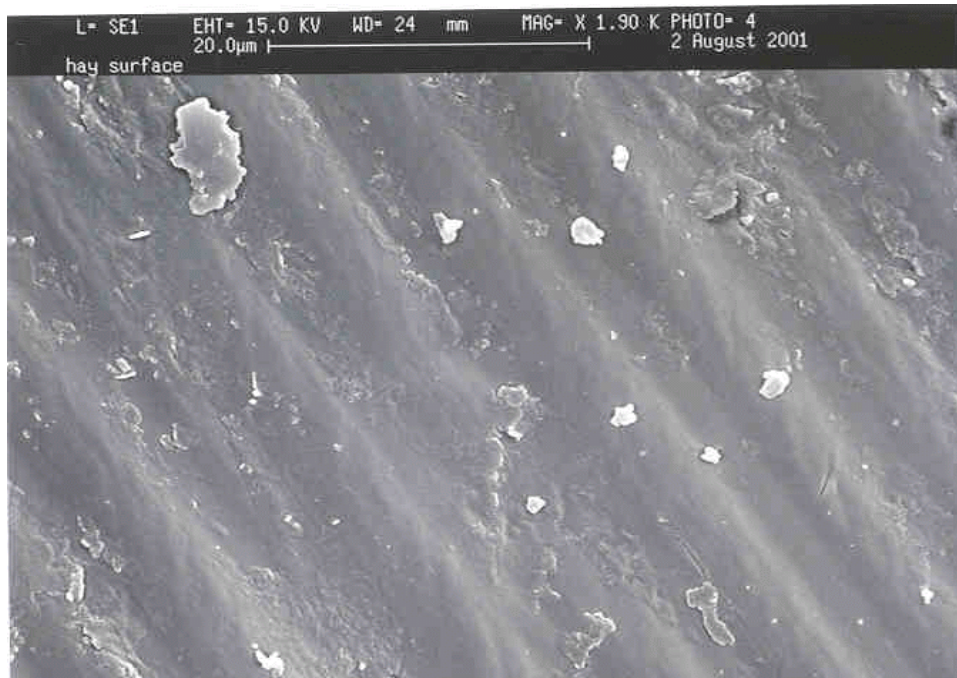
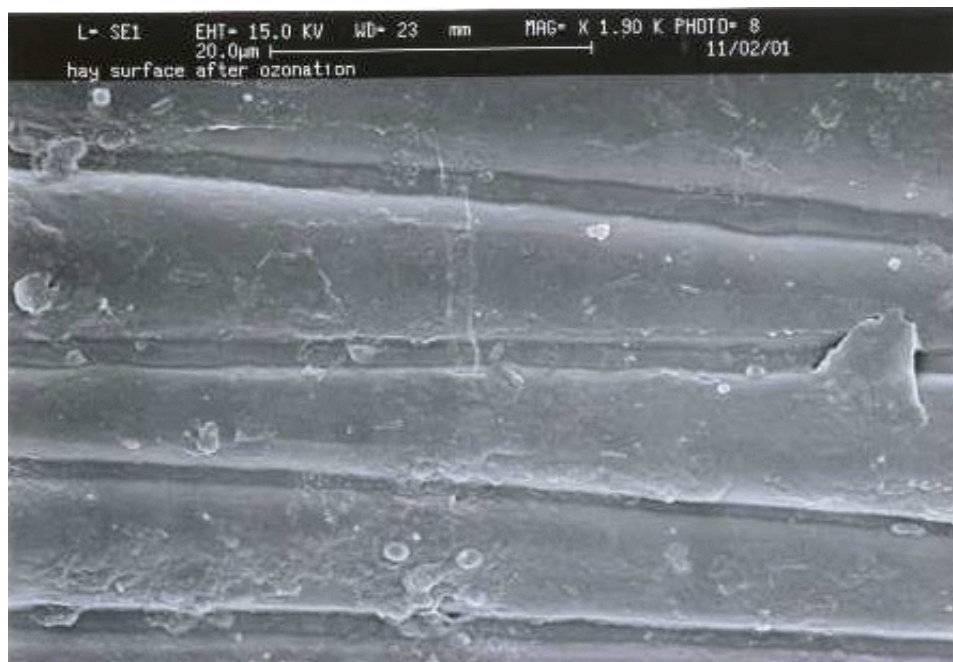Figure F.13. SEM micrograph of hay. Magnification: 1 x 1900.

Figure F.14. SEM micrograph of hay after ozone pretreatment.
Magnification: 1 x 1900.