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Treatment of organic and inorganic pollutants in municipal wastewater by agricultural by-product based granular activated carbons (GAC)

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TREATMENT OF ORGANIC AND INORGANIC POLLUTANTS IN MUNICIPAL
WASTEWATER BY AGRICULTURAL BY-PRODUCT BASED GRANULAR
ACTIVATED CARBONS (GAC)

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The objective of this investigation was to evaluate pecan and almond shell-based granular activated carbon's viability to effectively remove organic and inorganic pollutants in municipal wastewater compared to commercial carbons, Filtrasorb 200 (bituminous coal-based), and GRC-20, 206C AW (coconut shell-based). The solution to the objective was approached under three distinct phases, namely (I) physical and chemical characterization of the pecan and almond shell-based experimental and bituminous coal and coconut shell-based commercial granular activated carbons; (II) treatment of organic contaminants in municipal wastewater by experimental and commercial GACs; (III) treatment of inorganic contaminants in municipal wastewater by experimental and commercial GACs.

Phase I study showed that the almond shell-based chemically activated carbon (ALA) had the largest total surface area (1340 m^2/g) including the commercial carbons. The bulk densities of both physically and chemically (0.49 to 0.57 g/m^3) -activated pecan shell-based carbons were comparable to those of commercial carbons (0.49 to 0.54 g/m^3). ALA had the highest attrition (31.68%) compared to chemically activated pecan shell-based carbon (PSA) with lowest attrition (7.10%). PSA also contained the lowest ash, a desirable attribute. Activation affected conductivity. Chemical activation lowered conductivity when compared to physical activation. Multivariate analysis showed that steam- and acid-activated pecan shell-based carbons (PSS and PSA) had more similarity to commercial carbons.

Phase II study showed that PSS had higher adsorptive capacity towards Chemical Oxygen Demand (COD) than carbon dioxide-activated pecan shell-based carbon (PSC)

and commercial carbons. Activation methods of the carbons affected the pH. The study on adsorption of volatile organic compounds (VOCs) showed that all the experimental carbons exhibited efficient adsorbability of benzene and other halogenated aliphatic compounds under study. Multivariate analysis indicated, PSS and PSA to be similar in terms of overall VOC adsorption.

Phase III study showed that the PSS with higher log x/m (solute adsorbed/ carbon dosage) ratio and log Ce ranging from 0.5 to 1.0 g/100 ml is most suitable for the adsorption of Cu^{2+}. However, within the four carbons used for the adsorption of Pb^{2+} and Zn^{2+}, PSA was found to be more effective compared to PSS and PSC.

CHAPTER 1
INTRODUCTION

Municipal wastewater comprises of domestic (or sanitary), industrial wastewaters, infiltration and inflow into sewer lines, and stormwater runoffs. The characteristics of municipal wastewaters vary from location to location depending upon the sources of discharge, the effluents from industries, land uses, groundwater levels, and degree of separation between stormwater and sanitary wastes. Domestic wastewater includes typical wastes from the kitchen, bathroom, laundry, as well as any other wastes that people may accidentally or intentionally pour down the drain. Industrial effluents originate from product processing or cooling water. Infiltration; inflow; and or/ storm water runoff also contribute to the pollutant load of municipal wastewaters.

In the late 1950's, the U.S. Public Health Service- the federal agency then responsible for both water supply and pollution control- identified two major and convergent national problems; namely, increased water demand in the face of an essentially fixed fresh water supply and increased pollution of existing supplies by inadequately treated waste discharge (Weber, 1981).

In the past two decades, more than $ 75 billion in Federal, State, and local funds were used to construct municipal sewage treatment facility and the private sector has spent additional billions of dollars to limit discharge of conventional pollution (Liu and Liptak, 2000).

Municipal wastewater is characterized by its physical attributes as well as its organic and inorganic contaminants. Physical attributes include color, odor, and turbidity caused by dissolved or suspended solids. Organic contaminants include dissolved or undissolved VOCs which include phenols, chlorobenzene, hydrocarbons and dissolved or

undissolved non-volatile organic compounds designated as biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) such as carbohydrates, fats, starches etc., Inorganic pollutants may include compounds of trace minerals, sulfides, chlorides, nitrogen and phosphorous.

At present, municipal wastewater undergoes primary, secondary and tertiary treatments before it is discharged either for domestic or industrial uses. Primary treatment includes screening the wastewater for removing the suspended large or small particles, settling and skimming the oil from the top layer in the wastewater in the settling tanks. After the primary treatment, the wastewater undergoes secondary treatment, which may be one or more combinations of treatments by activated sludge, filters or lagoons. Secondary treatment is mostly a biological process wherein microorganisms in wastewater convert the non-settleable solids to settleable solids. Following the secondary treatments, the wastewater undergoes a tertiary treatment, which may be physical, chemical, biological or a combination of one or more of these preceding methods. However, in most instances physical method alone has been found to be sufficient to successfully complete the tertiary treatments. The physical treatments include membrane separation, chemical coagulation or adsorption by activated carbon, which has found wide applications in wastewater treatments. Adsorption by activated carbons is preferred because of its large surface areas resulting in higher separation efficiency. Activated carbon has low sensitivity to flow fluctuations and exhibits greater flexibility. Activated carbon is also used in water treatment plants for the removal of odors and tastes. Increasing requirements for cleaner and more polished effluent from

many processes suggests that, barring the development of new technologies; industrial need for activated carbon will only increase in the future.

Bone char, which is made by carbonizing specially selected sun-dried cattle bones can serve as an alternate to activated carbon. It has about 10% carbon and 90% calcium phosphate (hydroxyapatite) and has a bulk cost of $0.55 to $0.65 per lb. However, bone char is primarily a product imported from Brazil and India, and its cost and supply can vary according to the political situation in the supplying countries. Activated carbons, on the other hand can be made from agricultural byproducts, a renewable resource. Furthermore, abundance and the availability of low cost agricultural byproducts make them good candidates as precursors for activated carbons. Preliminary studies on cost estimation have shown that agricultural byproduct based activated carbons can be manufactured for as low as $0.45 per lb (Ahmedna et al., 2000(b)).

Studies by Ahmedna et al., (1997); 2000(a)) have shown that agricultural byproduct based granular activated carbons (GACs) derived from pecan shells and sugarcane bagasse have the potential for use in sugar refinery. Ng, (2001) demonstrated that pecan shell and sugarcane bagasse based GACs can effectively bind geosmin and may have the potential to control the off odor and flavor in farm-raised catfish. Pendyal et al, (1999) and Ahmedna et al., (1998) showed that GAC prepared from pecan shell and sugarcane bagasse resemble in their physical and chemical properties very closely to commercial activated carbon such as Filtrasorb 400.

A comprehensive review of the literature showed no published literature on the use of agricultural by-product based GAC for treating municipal wastewater. Therefore the present investigation was initiated with the following objectives:

(1) To characterize the physical and chemical characteristics of agriculture based granular activated carbons such as those from pecan and almond shells, and compare these characteristics to the characteristics of commercial carbons such as Calgon Filtrasorb 200, Calgon GRC-20, and Waterlinks 206C AW.

(2) Evaluate whether or not agricultural byproduct-based granular activated carbons (GACs) such as those prepared from pecan shells and almond shells can be used as adsorbents in municipal wastewater treatments for removing inorganic and organic pollutants, and to compare the adsorption efficiencies of the agricultural byproduct-based GACs to the adsorption efficiencies of widely used commercial carbons such as Filtrasorb-200 (Calgon Carbon Corporation).

In order to accomplish these objectives, seven activated carbons consisting of four experimental carbons, namely (i) Pecan shell-steam activated (ii) Pecan shell-carbon dioxide activated (iii) Pecan shell-acid activated carbons, and (iv) Almond shell-acid activated and three commercial carbons, namely (v) Calgon Filtrasorb-200 (vi) Calgon GRC-20, coconut-based activated carbon and (vii) Waterlinks 206C AW, coconut-based activated carbon were tested for their adsorption efficiencies in a simulated standard solutions (to minimize experimental errors caused by interfering ingredients) containing inorganic and organic species. The results obtained with respect to the physical and chemical properties of the GACs used in this study are presented in chapter 3 and the results obtained on the effectiveness and adsorption efficiencies of experimental and commercial carbons with respect to organic pollutants are presented in Chapter 4. The data corresponding to the removal of inorganic pollutants is presented in Chapter 5.

CHAPTER 2
LITERATURE REVIEW

2.1 Municipal Wastewater Sources and Characteristics

The characteristics of wastewater discharges vary from location to location depending upon the population and industrial sector served namely, land uses, groundwater levels, and degree of separation between stormwater and sanitary wastes. Domestic wastewater includes typical wastes from the kitchen, bathroom, and laundry, as well as any other wastes that people may accidentally or intentionally pour down the drain. Sanitary wastewater consists of domestic wastewater as well as those discharged from commercial, institutional, and similar facilities. In general, the volume of sanitary wastewater generated is about 400 liters per capita per day. An industrial waste is as varied as the industry that generates the waste. The quantities of storm water that combines with domestic wastewater vary with the degree of separation that exists between the storm sewers and the sanitary sewers. Most new sewerage systems collect sanitary wastewater and storm wastes separately, whereas older combined systems collect both sanitary wastewater and storm water together.

Physically, wastewater is usually characterized by a gray color, musty odor, and a solids content of about 0.1%. From a physical point of view the suspended solids can lead to the development of sludge deposits and anaerobic conditions when discharged into the receiving environment.

Chemically, wastewater is composed of organic and inorganic compounds as well as various gases. Organic components may consist of carbohydrates, proteins, fats, greases, surfactants, oils, pesticides, phenols, etc., Inorganic components may consist of heavy metals, nitrogen, phosphorus, sulfur, chlorides etc. In domestic wastewater, the

organic and inorganic portions are approximately 50% for each category (Liu and Liptak, 2000). However, since wastewater contains a higher portion of dissolved solids than suspended, about 85 to 90% of the total inorganic component is dissolved and about 55 to 60% of the total organic component is dissolved. Gases commonly dissolved in wastewater are hydrogen sulfide, methane, ammonia, oxygen, carbon dioxide, and nitrogen. The first three gases result from the decomposition of organic matter present in the wastewater.

Biologically, wastewater contains various microorganisms but the ones that are of concern are those classified as protista, plants, and animals. The category of protista includes bacteria, fungi, protozoa, and algae. Toxics compounds generated by the protista and found in wastewater pass through wastewater treatment facilities that have not been designed to remove them and can interfere with their operation. In a biological treatment process, these compounds can upset a treatment process or even kill the biological community and make the process ineffective (Liu and Liptak, 2000).

2.2 Municipal Wastewater Treatment

Generally most municipal wastewater treatment plants have primary and secondary treatment facilities followed by a tertiary processing plant. Primary treatment involves physical separation of floatable and settleable solids. Secondary treatment involves biological removal of dissolved solids. Tertiary treatment involves physical, chemical, and biological treatment.

2.2.1 Primary Treatment

This treatment involves the following processes, (i) screening-to remove large objects, such as stones or sticks, that could plug lines or block tank inlets, (ii) Grit

chambers- to slow down the flow to allow grit to fall out, and (iii) sediment tank (settling tank or clarifier) settleable solids settle out and are pumped away, while oil floats to the top and is skimmed off.

2.2.2 Secondary Treatment

Secondary treatment typically utilizes a biological treatment process; in which microorganism convert non-settleable solids to settleable solids. The secondary treatment includes: (i) activated sludges, (ii) tertiary filters and (iii) lagoons.

(i) Activated Sludge

Activated sludge treatment process commonly uses microorganisms to breakdown organism materials with aeration and agitation. A bacterium converting activated sludge is continually recirculated back to the aeration basin to increase the rate of organic decomposition allowing the solids to settle.

(ii) Trickling Filters

In trickling filters process, wastewater is sprayed into the air (aeration), consisting of beds of coarse media 3-10 ft deep. Microorganisms, attached to and growing on the media; breakdown organic material in the wastewater. Trickling filters drain at the bottom and the wastewater is collected and then undergoes sedimentation.

(iii) Lagoons

Lagoons rely mainly on interaction of sunlight, algae, microorganism, and oxygen (along with aeration). It is relatively cheap and inefficient.

2.2.3 Tertiary Treatment

After primary and secondary treatment, the municipal wastewater is subjected to tertiary treatment. This process includes physical and chemical treatments. Physical

processes consist of electrodialysis, reverse osmosis, carbon adsorption, and centrifugation. Chemical process involves hydrolysis, ozonation, precipitation, coagulation, and flocculation. The most common types of tertiary treatment methods are the following:

(i) Physico-chemical Treatment (PCT) Using Activated Carbon

The treatment uses granular carbon in the form of a bed. Wastewater flows through this bed, and the organic molecules are adsorbed on the carbon surface. The carbon is removed and regenerated when it becomes loaded with the adsorbed molecules and losses its adsorptive ability (Liu and Liptak, 2000).

(ii) Flocculation

The purpose of flocculation is to bring coagulated particles together by mechanically inducing a velocity gradient within a liquid. Organic polyelectrolyte flocculation aids are effective in promoting soluble solids removal. Flocculation improves the removal of finely divided solids by gravity settling.

(iii) Coagulation

Coagulation is the conversion of finely dispersed colloids into a small floc with the addition of electrolytes like inorganic acids, bases, and salts. Coagulation can either be followed by the process of settling or flotation.

(iv) Membrane Filtration

Porous membranes with flux rates (hydraulic loading) over 500 gpd per ft^2 at 50 psig are used to polish effluents from other filters. This type of filtration mainly involves ultrafiltration and hyperfiltration (reverse osmosis). Ultrafiltration membranes are

capable of rejecting high molecular weight compounds, soluble or organic substances, but are unsuccessful in removing salts.

(v) Hyperfiltration

Hyperfiltration uses specially prepared membranes or hollow fibers. It affects removal of salts, soluble organics matter, colloidal or soluble silica, and phosphates with a removal efficiency of 80-95 % (Faust and Aly, 1998).

2.3 Use of Activated Carbon Adsorption for Tertiary Treatment

As explained in section 2.2.3 above, activated carbon is extensively used in wastewater treatment. It is mainly used in tertiary treatment as a physico-chemical agent. Granular activated carbon is used in the form of a filtration bed. Wastewater flows through this bed and organic molecules are adsorbed on the carbon surface. When the carbon becomes loaded with the adsorbed molecules and loses its adsorptive ability, it can be removed from the system and regenerated. Most commonly used commercial carbon for this process is made from bituminous coal (Faust and Aly, 1998).

The advantages of using granular activated carbon for physico-chemical treatment are: (1) reduced land area requirement (less than half) when compared to biological treatment plants, (2) higher levels of wastewater treatment efficiency as compared to conventional biological processes, (3) reduced sensitivity to daily flow variations, (4) greater design flexibility, and (5) greater operational flexibility and control (Eckenfelder, 1981).

Certain organic compounds in wastewater are resistant to biological degradation and contribute for the bad odor, taste, or color of the water. Even at low concentration, they are not readily removed by conventional treatment methods. Activated carbon has

an affinity for organics and its use for organic contaminants removal from wastewater is widespread. The effectiveness of activated carbon for the removal of organic compounds from wastewater by adsorption is enhanced by its large surface area, a critical factor in the adsorption process. The adsorption rate is influenced by carbon particle size, but not the adsorptive capacity, which is related to the total surface area.

Granular activated carbon is also used for providing tertiary treatment following conventional biological treatment. In this case, the carbon exhaustion rate usually ranges from 0.01– 0.06 g/l (0.1 – 0.5 lb/1000 gal). Contact time ranges from 15 – 30 min. As in the case of secondary treatment, the granular carbon can be used for filtration as well as adsorption, or prefilters can be provided.

Granular activated carbon has been used to remove organics from a wide range of industrial wastewater including dyes, phenolics, benzene, and chlorinated hydrocarbons. Many of these organics are toxic and not amenable to alternative biological process. The carbon exhaustion rate for industrial application can range from as low as 50 kg/day (110 lb/day) to greater than 50,000 kg/day (110,000 lb/day) depending on the type and concentration of contaminant, effluent objective, adsorber configuration, and contact time. Contact times will generally range from 30 –100 min (Hassler, 1963).

2.4 Agricultural By-product Based Granular Activated Carbon

Surplus, low value agricultural by-products can be made into granular activated carbon (GAC), which is used, in environmental remediation. The by-products include soft lignocellulosics such as rice straw, soybean hull, sugarcane bagasse, peanut shell and harder materials such as pecan and walnut shells. The production of granular activated carbon (GAC) from agricultural by-products serves a double purpose. First, unwanted,

surplus agriculture waste, of which billions of kilograms are produced annually, is converted to useful, value-added adsorbents (Johns et al., 1998). Thus, the use of agricultural by-products represents a potential source of novel GACs, which may be effective and contribute to solving many current, environmental pollution problems. Nutshells have been reported in previous studies to be a good alternative to coal as feedstock for the production of GAC. Renewable resources, such as nutshells, were desirable as carbon precursors because of their low ash content, and high bulk density (Wartelle and Marshall, 2001).

The adsorptive capability of activated carbon depends on the process of activation; pore size distribution and surface characteristics. GAC has been shown to effectively remove phenolics, polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), synthetic organic chemicals (SOCs), certain low-level metals, and BTEX (benzene, toluene, ethyl benzene, and p-xylene). In addition, oxidants, such as hypochlorous acid (HOCl), hydrogen peroxide (H_2O_2) and ozone (O_3) are eliminated by GAC (Butterworth and Sember, 1993). The adsorptive capacity of activated carbon is determined, not only by its total surface area, but also by its internal porous structure and the presence of functional group on the porous surface (Ahmedna et al., 2000(b)). The electrical charge of the surface group may also enhance or hinder the adsorption of the target molecules on the carbon surface.

2.5 Manufacturing Activated Carbon

Activated carbon has been produced mainly from high carbon content material such as wood, coal, peat, lignin, nutshells, sawdust, bone, and petroleum coke. The production of activated carbon involves two processes, namely, carbonization, followed

by activation. Before carbonization and activation, the starting materials are adjusted to exhibit the desired final physical properties such as granule size, shape, roughness, and hardness. These properties are influenced by production techniques. Blends of the pulverized material and binders (sugar, tar, pitch, and lignin) are often used to obtain desired particle size during extrusion.

Carbonization or pyrolysis consists of slow heating of the material at temperatures usually below 800ºC in the absence of air. During this stage of pyrolysis, volatile products are removed from the starting material. Carbonization can sometimes be controlled by addition of dehydrating agents such as zinc chloride or phosphoric acid, which are recovered for reuse. Activation consists of treating the pyrolized char with activating agents such as steam or carbon dioxide at elevated temperatures, 800-900ºC, that transforms the char into numerous pores which are systematically developed and enlarged, thus enabling the production of a well defined pore system in the activated carbons.

During activation, the surface area or adsorption is determined by (1) the chemical nature and concentration of the activating agent, (2) the temperature of the reaction, (3) the extent to which the activation is conducted, and (4) the amount and kind of mineral ingredients in the char.

Temperature must be high enough to provide a reasonably rapid rate of activation, but temperatures above 1000ºC are to be avoided because they begin to impair adsorption. Activation with steam or carbon dioxide is conducted at temperatures from 800º to 900ºC. Activation with air involves an exothermic reaction and measures must be taken to keep the temperature from rising above proper limits – usually not over 600ºC.

Other activation processes include the use of dolomite, sulfates, phosphoric acid, sodium and potassium hydroxides, thiocyanates, sulfide, and potassium and sodium carbonates (Hassler, 1963).

2.6 Types of Activated Carbons

2.6.1 Powdered Activated Carbon

After activation, carbon intended for batch treatment of liquid systems is pulverized to a suitable size. Most activation processes produce a carbon with a pH > 7 an alkaline, although some processes produce an acid carbon. The pH can be adjusted by supplementary addition of acid or alkali to meet the varied needs of different industrial users. When the intended use requires low ash content with low conductivity, the carbon is washed with water, or with acid and then with water.

2.6.2 Granular Activated Carbon

GAC is used in columns or beds for gas and vapor systems, and also for processing a number of liquids. The carbon must possess sufficient mechanical strength to withstand the abrasion incident to continued use. The development of high adsorptive power is accompanied by loss of mechanical strength and density. Therefore the activation stage cannot be too short because the carbon would lack needed adsorptive power; conversely, it cannot be too long for then the carbon would be too soft and bulky.

Few materials, in their natural state, can be converted into activated carbon with high density and low attrition. Less dense material, however, can be made dense and yield a hard carbon when mixed with a binder. The binder should be a substance which when carbonized does not liquefy or expand. However, some shrinkage is desirable. The tarry by-products from woods and certain grades of anthracite and bituminous coal have

been found to be good binders. To be suitable as a binder, a substance should liquefy or soften during carbonization and swell sufficiently to give a porous structure. Suitable binders include sugars, tar, pitch, and lignin.

2.7 Adsorption Principles

Planar surface of the micropores contributes mostly to the surface area, which is responsible for the adsorptive property of the activated carbon. The adsorption on these surfaces is mostly physical due to weak Van der Waals forces. During the process of carbonization, a large number of unpaired electrons, which are resonance stabilized, are trapped in the microcrystalline structure.

2.7.1 Factors Affecting Adsorption

Surface Area, Pore Structure, and Pore Size Distribution

Surface area is one of the principle characteristics affecting the adsorptive capacity of an adsorbent, since the adsorption process results in a concentration of solutes at the surface.

Pore structure and chemistry of activated carbon made from agricultural by-products are strongly dependent on pyrolysis temperature, composition, and structure of the raw material (Girgis et al., 1994).

Most of the macropores are formed during the pyrolysis process in the void volume filled by the binder. The shaping process of the granules determines the macropore system. Granule size depends on the forming pressure, particle size and particle size distribution of the starting material in the granule. Since surface properties of the GAC are a function of the precursor, pyrolysis and activation conditions, it is essential to characterize them with respect to the number and type of the chemical group

14

on the surface, the polarity of the surface, pore size distribution and total surface area. (Ahmedna et al., 2000(b)).

Particle Size

Activated carbon is a complex network of pores of varied shapes and sizes. The shape includes cylinders, rectangular cross sections, as well as many irregular shapes and constrictions. The size can range from less than 10 Å to over 100,000 Å. Pore size distributions; will depend on the source materials used and on the method and extent of activation. Pores are often classified as macropores, mesopores, and micropores (Hassler, 1963).

Chemistry of the Surface

There are two methods of adsorption, namely, physisorption and chemisorption. Both methods take place when the molecules in the liquid phase becomes attached to a surface of the solid as a result of the attractive forces at the solid surface (adsorbent), overcoming the kinetic energy of the contaminant (adsorbate) molecules.

Physisorption occurs, as a result of energy differences and/or electrical attractive forces (weak Van der Waals forces), the adsorbate molecules become physically fastened to the adsorbent molecules. This type of adsorption is multi-layered; that is, each molecular layer forms on the top of the previous layer with the number of layers being proportional to the contaminant concentration. More molecular layers form with higher concentrations of contaminants in solution.

When a chemical bond is produced by the reaction between the adsorbed molecule and the adsorbent, chemisorption has occurred. Unlike physisorption, this process is one molecule thick and irreversible, because energy is required to form the

new chemical compounds at the surface of the adsorbent, and energy would be necessary to reverse the process. The reversibility of physisorption is dependent on the strength of attractive forces between adsorbate and adsorbent. If these forces are weak, desorption is readily affected.

Factors affecting adsorption include:

1. The physical and chemical characteristics of the adsorbent, i.e., surface area, pore size, chemical composition, etc;

2. The physical and chemical characteristics of the adsorbate, i.e., molecular polarity, chemical composition, etc;

3. The concentration of the adsorbate in the liquid phase (solution)

4. The characteristics of the liquid phase, i.e., pH, temperature, and

5. The residence time of the system.

2.8 Nature of the Adsorbate

2.8.1 Effect of pH

The adsorption of non-electrolytes by activated carbon from aqueous systems is generally not affected by the solution pH, although some exceptions can occur. However, the effect of pH on the adsorption of weak electrolytes, both acids and bases, is quite pronounced. Both undissociated and ionized form of a species can be adsorbed on activated carbon, with undissociated form being more strongly adsorbed than ionized forms (Faust and Aly, 1998).

2.8.2 Effect of Inorganic Ions

The inorganic composition (Ca^{2+}, Mg^{2+}, etc) of water can also have an important effect on adsorption of selected organics from water by activated carbon. Calcium ion

complexes with the carbon, which increases Ca^{2+} adsorption. Many other divalent cations can act in similar manner, but Ca^{2+} has special interest because of its ubiquitous distribution in natural water. Other inorganic ions include Cu^{2+}, Zn^{2+}, Ag^{2+}, and Pb^{2+} commonly found as contaminants in wastewater.

2.8.3 Effects of Temperature

Since the process of adsorption is spontaneous, it is accompanied by a decrease in the system's free energy. There is always a decrease in entropy due to loss of degree of freedom of the solute in passing from the dissolved state to the adsorbed state. The decrease in entropy drives a decrease in enthalpy (ΔH) where the two are related by.

$$\Delta H = \Delta G + T\Delta S$$

The enthalpy change (ΔH), for physical adsorption is in the range of 2-15 kcal/mol. An increase in temperature therefore results in a reduction of the equilibrium adsorptive capacity.

2.9 Adsorption Equilibria

Adsorption from aqueous solutions involves concentration of the solute on the surface. As the adsorption process proceeds, the sorbed solute tends to desorb into the solution. Equal amounts of solute eventually are being adsorbed and desorbed simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state. The position of equilibrium is characteristic of the solute, adsorbent, solvent, temperature, and pH. Several models are used for the description of the adsorption data of which the Langmuir and Freundlich models are the ones most commonly used.

2.9.1 Langmuir Adsorption Isotherm

Langmuir's model is characterized by the following conditions:

1) The molecules are adsorbed on definite sites on the surface of the adsorbent; 2) each site can accommodate only one molecule (monolayer); 3) the area of each site is a fixed quantity determined solely by the geometry of the surface; and 4) the adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir adsorption isotherm is expressed as:

$$X = \frac{X_m b C_e}{1 + b C_e}$$

Where X = x/m, the amount of solute adsorbed x per unit weight of adsorbent m

C_e = equilibrium concentration of the solute

X_m = amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity

b = a constant related to the heat of adsorption $Q = \left[b e^{(-H/RT)} \right]$. This equation can be written in the form:

$$C_e = \frac{1}{b X_m} + \frac{C_e}{X_m}$$

When C_e/X is plotted vs. C_e a straight line, should result, having a slope $1/X_m$ and an intercept $1/bX_m$. The monolayer capacity X_m determined from the Langmuir isotherms defines the total capacity of the adsorbent for a specific adsorbate.

2.9.2 Freundlich Adsorption Isotherm

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as:

$$\frac{x}{m} = kC_e^{1/n}$$

Where, x = the amount of solute adsorbed

m = the weight of adsorbent

C_e = the solute equilibrium concentration

k, 1/n = constants characteristic of the system

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e$$

Plotting log x/m vs. log C_e, a straight line is obtained with slope of 1/n, and log k is the intercept of log x/m at log C_e =0 (C_e= 0). The value of 1/n obtained for adsorption of most organic compounds by activated carbon is < 1. The Freundlich equation indicates the adsorptive capacity or loading factor on the carbon, x/m, is a function of equilibrium concentration of the solute. Therefore higher capacities are obtained at higher equilibrium concentrations.

2.10 Removal of Organic Pollutants

The ability of granular activated carbon to remove a broad spectrum of organic compounds from water is well documented (Toles, et al., 2000, 1998, 1997; Johns, et al., 1998; Dastgheib and Rockstraw, 2001; Wartelle, et al., 2001). In recent decades the quality of many water supplies has been adversely affected by factors associated with the tremendous growth in the production of industrial chemicals.

Many of the contaminants are highly stabilized organic compounds that are not destroyed by biological or chemical treatment of wastes, and they often survive the self-purification that normally occurs in moving streams. The organic contaminants are not appreciably removed by the steps of coagulation, chlorination, and filtration employed in water purification plants. Activated carbon is used in sufficient quantities to make the water palatable and eliminate foamining, and only the more odorous ingredients will give a perceptible taste at the dilutions usually present.

Some organic contaminants are more adsorbable than others. Organic solvents such as trichloethylene and aromatic solvents such as toluene are adsorbable due to their low solubility in water. Higher molecular weight compounds, such as polynuclear aromatics, and surfactants, are also effectively adsorbed. Conversely, water-soluble compounds such as alcohols and aldehydes are poorly adsorbed (Stenzel, 1993). Volatile organic compounds (VOC) such as low molecular weight chlorinated solvents and aromatics are generally treated with air stripping or granular activated carbon. Air stripping yields 95-99% removal of VOCs. However due to environmental issues, discharge of VOCs into the atmosphere limits its utility. Granular activated carbon on the other hand can remove both volatile as well as non-volatile compounds with effective reduction of organic contaminants to undetectable limits and prevent their discharge back in atmosphere (Stenzel, 1995).

2.11 Removal of Inorganic Pollutants

Toxic metal compounds not only contaminate surface water sources (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amounts by leaching from the soil after rain and snow. Toxicity of heavy metals has triggered a

number of studies aimed at removal of the metal ions from aqueous solutions. In treatment of wastewater streams containing heavy metals, precipitation is a commonly used treatment approach. However, the effectiveness of precipitation depends strongly on the composition of the wastewater. In addition, precipitation produces sludge that requires further treatment. Ion exchange and adsorption have been alternative methods for removing metals.

In the past, most studies focused on the adsorption equilibrium of single-species metal ions, while less result appeared in the literature on multi-species metal adsorption. In addition, a survey of the relevant literature on adsorption of heavy metals onto activated carbon shows that the adsorption kinetics and its modeling simulation have not been thoroughly studied.

CHAPTER 3
PHYSICAL AND CHEMICAL CHARACTERIZATION OF PECAN AND ALMOND SHELL-BASED GRANULAR ACTIVATED CARBONS (GACs) AS ALTERNATIVE TO COMMERCIAL CARBONS IN MUNICIPAL WASTEWATER

3.1 Introduction

The production of granular activated carbons (GACs) from agricultural by-products in recent years has served not only to convert unwanted, surplus agriculture waste, which are produced in millions of tons annually but also been successfully used as a cheap viable remediation bio-utility and value-added adsorbents. In recent years various applications of the granular activated carbons from agricultural by-products have been published and include for raw sugar decolorization (Ahmedna, et al., 2000 (a), 2000(b)), metal and organic adsorption capacities (Toles, et al., 2000, 1998, 1997; Johns, et al., 1998; Dastgheib and Rockstraw, 2001; Wartelle, et al., 2001), geosmin adsorption ability in water (Ng, et al., 2001), as a purge-and-trap gas chromatographic analyte for determination of volatile organic compounds (Wartelle, et al., 2000). The physical, chemical, and surface properties have also been extensively characterized (Johns, et al., 1999; Ahmedna, et al., 2000 (c); Toles, et al., 1999, 2000) in order to better understand the carbons adsorption properties.

The adsorption efficiency of the granular activated carbon is greatly affected by their physical properties such as total surface area, bulk density, attrition/ hardness, and chemical properties, which include pH, ash content, and conductivity.

Total surface area is the most important property in the separation by adsorption of organic and inorganic molecules, as large amount of surface porosity has large capacity to adsorb organic and inorganic molecules from liquid or gases (Smisek and

Cerny, 1970). Surface area of activated carbons is mostly macro and microporous (Najm, et al., 1980). The total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species (Ahmedna, 1998).

Bulk density is an important criterion for consideration in the designing of adsorption towers for use in pilot plant studies as well as large commercial applications. The adsorption rate is influenced by carbon particle size, which again depends on the bulk density of the granular activated carbon. During municipal wastewater treatment the residence time of the wastewater in the column containing granular activated carbon is affected by the bulk density (ρ) as shown by the equation:

$$R_s = \frac{\rho A v r}{7.48T}$$

where,

R_s = carbon usage rate (lb/ft^2 min)

ρ = bulk density of the GAC (lb/ft^3)

A = adsorber cross-section area (lb/ft^2)

v = linear flow rate (gallons/min/ft^2)

r = residence time (min.), and

T = processing time (Perrich, 1981).

Attrition or hardness measures the mechanical strength and determines their ability to withstand normal handling operations. Granular activated carbons used for any separation process including municipal wastewater treatment are exposed to a variety of external forces during shipping, loading into adsorption beds, and backwashing, which causes crushing on impact, granule-to-granule abrasion, and the generation of undesirable fines (AWWA, 1991). The carbon upon subsequent commercial usage requires

23

regeneration, which involves removing the adsorbate and simultaneously reestablishing the original adsorptive capacity of the virgin carbon (Faust and Aly, 1998). During the regeneration process some losses usually occur due to burn off and mechanical attrition, and it is therefore desirable to have lower attrition values for carbon.

Ash content is the measure of minerals present as impurities in the carbon. They are the residues, which remain upon burn off of the carbonaceous portion during pyrolysis. The ash content of the activated carbon depends on the precursor and is positively correlated to pH (Ahmedna et al., 2000 (a)). Therefore materials with lowest ash content precursor are preferred in order to have the most active sites on the surface of the granular activated carbon.

The pH of the activated carbon affects the adsorptive property of the carbons, as highly acidic or basic carbons are undesirable for processing. The pH of the granular activated carbons is influenced by the ash content. Generally, neutral pH is preferred for the municipal wastewater treatment as higher or lower pH affects the adsorption process and influences the pH of the treated water.

Conductivity measures the leachable minerals. These minerals may cause specific problems with catalysis of adverse reactions or interference by competitive adsorption (Ng, 2001). In order to improve the adsorption performance the activated carbon with higher conductivity will have to be prewashed making the treatment process cumbersome and expensive. Therefore it is desirable to use activated carbon with low conductivity in wastewater treatment processes.

Abundance and low cost make agricultural by-product good candidates as precursor of the activated carbons. By-product based GACs, besides helping minimize

environmental pollution, creates new value added products, which offer additional marketing opportunities to farmers and processors. The major raw materials which have been shown to be suitable for the manufacture of granular activated carbons are peat, peat moss, bituminous coal, bone char, lignite, coconut shells, sugarcane bagasse, and rice hulls. However raw materials such as bagasse, rice hulls consists of soft compressible waste products of low density and need binders, whereas shells from nuts such as coconut are hard, dense and not easily compressed and does not need a binder. Other nutshells, which have drawn attention of investigators as potential precursors for granular activated carbons, include pecan, macadamia nuts, walnut, and almond. GACs prepared from nutshells have been shown to be economically competitive compared to coal based and bone char based carbons (Ng, 2001).

The nutshell based granular activated carbons are preferred as a precursor due to their hardness, as mentioned previously; they do not require binder during manufacturing of the granular activated carbons. It was reported by johns et al., (1999) that the total pecan shell annual production accounted for 61,000 metric tons and Toles et al., (2000) reported the almond production of 236,000 metric tons,both in the United States alone. The use of nutshell in the production of GAC potentially provide a less expensive raw material than the coal presently used, as well as producing a GAC manufactured from a renewable resource instead of a non renewable resource. These agricultural by-products could thereby be used as renewable resources, as they are desirable for carbon precursors because of their low ash content, and high bulk density (Wartelle and Marshall, 2001).

Activated carbon is extensively used in municipal wastewater treatment as a physico-chemical agent in tertiary treatment. Granular carbon is used in the form of a

filtration bed, where wastewater flows through this bed and organic molecules are adsorbed on the carbon surface. When the carbon becomes loaded with the adsorbed molecules and loses its adsorptive ability, it can be removed from the system and regenerated. Most commonly used commercial carbon for this process is made from bituminous coal (Faust and Aly, 1998) and bone char. These carbons either are non-renewable sources or are imported, subjecting to higher cost. Granular activated carbons on the other hand are prepared from domestic agriculture by-products, and are renewable source, besides being cost effective and viable alternative for waste disposal and reuse.

A comprehensive review of literature showed limited published information on the use of pecan and almond shell based granular activated carbons for wastewater treatment. However, few investigators have shown that the potential for this nutshell do exists in the preparation of GACs. Therefore the present investigation was initiated with the following objectives: (1) to characterize physically and chemically, pecan and almond shell-based granular activated carbons, activated physically by steam and carbon dioxide and chemically by nitric acid. (2) to compare the characteristics of these shell-based granular activated carbons to those characteristics of commercial granular activated carbons namely Filtrasorb 200 (F200), Calgon's coconut shell-based carbon (GRC-20), Waterlinks coconut shell-based based carbon (206C AW). These commercial carbons were selected because they are widely accepted as adsorbents in municipal wastewater systems and currently in use. The comparison of the physical and chemical characteristics of pecan and almond shell-based granular activated carbons to those of commercial carbons should help in suitable selection of nutshell based granular activated carbons.

3.2 Materials

The samples used in this study consisted of:

(A) Four experimental carbons, namely

    i. Pecan shell-based steam-activated

    ii. Pecan shell-based carbon dioxide-activated

    iii. Pecan shell-based acid-activated

    iv. Almond shell-based acid-activated

    These carbons were produced at USDA, Southern Regional Research Center, New Orleans, LA, and were furnished for analysis and

(B) Three commercial carbons, namely

    i. Filtrasorb-200

    ii. Calgon (Pittsburgh, PA) coconut shell-based activated carbon (GRC-20) and

    iii. Waterlinks (Barneby Sutcliffe, Ohio) coconut shell-based activated carbon (206C AW)

    These carbons were selected as a control for this experiment as they have found to possess the desirable physical and chemical characteristics and were extensively used in municipal wastewater treatment plants.

3.3 Methods

3.3.1 Measurement of Physical Properties of GACs

Total Surface Area (m²/g)

    The total surface area of the activated carbons was determined by the method Pendyal et al. (1999) using Micromeritics Gemini 2375 surface area analyzer

(Micrometrics Inc., Norcross, GA). The total surface area was measured by nitrogen adsorption at 77°K using 15 point BET (Braunauer et al., 1938).

Bulk Density (g/m^3)

Bulk density was measured using the method of Ahmedna et al. (1997), which consisted of placing a known weight of granular activated carbon of 10-30 mesh size carbon in a 25 ml cylinder to a specified volume and tapping the cylinder for at least 1-2 min. and measuring the volume of carbon. The bulk density was measured as:

Bulk density (g/m^3)= $$\frac{\text{weight of dry sample (g)}}{\text{volume of packed dry sample (g)}}$$

Attrition/ Hardness (%)

The attrition of the samples was measured using wet attrition method described by Toles et al. (2000). One gram of granular activated carbon of 10-30 mesh was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid, pH 4.8) in a 150 ml beaker. The solution was stirred at 500 rpm for 24 h using Variomag Electronic Ruhrer Multipoint HP 15 stirrer (Daytona Beach, FL) with a ½ inch stir bar for agitation. The solution was then filtered through 50- mesh screen and the retained carbon was thoroughly washed and dried at 90°C under vacuum for 4 h and weighed. The % attrition was measured as:

$$\text{Attrition (\%)} = \frac{\text{Initial weight (g)} - \text{Final weight (g)}}{\text{Initial weight (g)}} \times 100$$

3.3.2 Measurement of Chemical Properties of GACs

Ash Content (%)

Ash content was measured by weighing a 2g of powdered carbon (<325 mesh size) in a porcelain crucible and heating the carbon to 115°C for 16 h. The carbon was then heated in a muffle furnace at 950°C for 1.5 h. The crucible was then removed and placed in a dessicator and weighed after cooling. The ash content was calculated as:

Ash (%) =   Final solids weight (g)   x 100
                   Initial carbon weight (g)

pH of Activated Carbons

The pH was measured by suspending one gram of carbon in 100 ml distilled water at pH 7.0 and heating at 90°C for 20 min. The solution was then cooled and pH measured using Orion 410 pH meter (Orion research Inc., Cambridge, MA). The pH was calibrated prior to analysis by using standard buffer with in the range of the pH to be measured.

Conductivity (μS)

Conductivity was measured using method mentioned by Ahmedna et al., (1998). One gram of the carbon was suspended in distilled water for 20 min. and conductivity measured as mico-Siemen (μS) using HACH CO 150 Conductivity meter (Loveland, CO).

Statistical Analysis

Analysis of variance was carried out in order to measure the significant difference between experimental and commercial carbons with respect to the physical and chemical characteristics. Multivariate techniques such as Principal component analysis and cluster analysis were carried out to analyze the data in order to group the carbons based on their

physical and chemical properties, and combined properties.   Principal component

analysis (SAS, 1989) uses a scatter plot with four quadrants along the x and y-axis.   The

distribution of carbons based on their overall adsorptive properties was studied.   For

cluster analysis (SAS, 1989) non-hierarchical techniques was involved.   The statistical

interpretation was done using SAS 8.2 version software (SAS Institute Inc., NC).

3.4 Results and Discussion

3.4.1 Physical Properties of GACs

The experimental results obtained on the physical properties of the shell-based

GACs and the commercial carbons are presented in Table 3.1.

Total Surface Area: The adsorption efficiency of activated carbon is directly related to

the total surface area of the carbon. Larger the surface area, higher is the adsorption

efficiency of the carbon and hence an important attribute while considering the selection

of adsorbents in the separation process.

From the data shown on total surface area in Table 3.1, among the three

commercial carbons used, the coconut shell-based GRC-20 carbon, manufactured by

Calgon Corporation, had the largest total surface area with 1038 m^2/g, followed by

another coconut shell-based carbon 206C AW with 898 m^2/g, manufactured by

Waterlinks Corporation.   The lowest total surface area of 835 m^2/g found among the

commercial samples used in this investigation was of Filtrasorb-200 (F200), which is a

coal based carbon.

Among the shell based experimental carbons, almond shell-based chemically-

activated granular activated carbon (ALA) had the largest total surface area of any carbon

at 1340 m^2/g, followed by steam-activated pecan shell-based carbon with 917 m^2/g and

acid-activate pecan shell-based carbon 902 m^2/g and carbon dioxide-activated pecan shell-based carbon with 435 m^2/g. Comparison of the total surface area of the pecan and almond shell-based experimental carbons to the total surface area of the commercial carbons showed that almond shell-based chemically-activated carbon had significantly (5% significance) larger surface than F200 (Filtrasorb 200), GRC-20 (Calgon coconut shell-based carbon), and 206CV AW (Waterlinks coconut shell-based carbon). In regard to the effect of activation method on the total surface area of the carbon, independent of the precursor used, chemical activation produced the largest total surface area with 1340 m^2/g compared to the largest surface area of the steam-activated pecan shell-based carbon PSS. Steam-activated pecan shell-based carbon with second largest total surface area among the experimental carbon was significantly (5% significance) greater than the total surface area of either commercial carbons F200 (835 m^2/g) or 206C AW (898 m^2/g).

The results may indicate why acid and steam activation are preferred activation methods for commercial processes compared to carbon dioxide activation. Carbon dioxide is more expensive than steam in addition to yielding, a lower surface area under the same activation conditions of time and temperature.

Bulk Density: Bulk density, an important characteristic of the carbon and is related to the starting material. Bulk density is one of the variables in the design of adsorption columns, also affects the overall cost of the adsorption process. A higher density carbon will generally not have to be generated as frequently as it will hold more adsorbate per unit volume (U.S. Environmental Protection Agency, 1973).

The data on bulk density of the almond and pecan shell-based experimental GACs and the commercial carbons indicates, that the three commercial carbons used in this

investigation, 206C AW (Waterlinks Corporation) had the highest bulk density (0.54 g/m^3) followed by F200 (Filtrasorb 200) with 0.49 g/m^3 and GRC-20 (Calgon coconut shell-based carbon) with a value of 0.47 g/m^3. Since the bulk density is inversely related to the particle size, the carbon 206C AW with the highest bulk density had carbons with smaller particle size than the other two commercial carbons F200 and GRC-20. In regard to the bulk density of the experimental carbons, the data indicates that the carbon PSC (pecan shell-based physically-activated by carbon dioxide) had the highest value (0.57 g/m^3) followed by PSA (0.51 g/m^3), PSS (0.49 g/m^3), and ALA (0.3 g/m^3). Only the almond shell-based GAC had bulk density value lower than 0.49 g/m^3 (0.30 g/m^3). Almond shells are soft and less dense than pecan shell (Wartelle and Marshall, 2001) and therefore produce carbons of lower density.

Statistical analysis of the bulk density data of experimental and commercial carbons indicated that the bulk density of the ALA, experimental carbon was significantly (5% significance) greater than F200, GRC-20, and 206C AW. However, with in the pecan shells, physical activation by carbon dioxide had significantly (5% significance) positive affect on the bulk density compared to chemical activation by acid as reflected by the data in Table 3.1, that the bulk density of the carbon PSC to be 0.57 g/m^3 compared to that of PSA equal to 0.51 g/m^3. The overall bulk density result indicate that pecan shell-based granular activated carbon were comparable to the commercial carbons.

Attrition/ Hardness: is a measure of the mechanical strength of the carbons and is an important parameter for understanding its relative loss during transportation, handling, and regeneration.

The results indicate that commercial carbons displayed lower attrition than the nutshell based carbons. F200 with a value of 3.26 % had the lowest attrition when compared to GRC-20 (7.27 %) and 206C AW (7.26 %) among the commercial carbons. Both the coconut shell-based commercial carbons GRC-20 and 206C AW showed comparable attrition values. The lowest attrition in the commercial carbons (F200) was bituminous coal based carbon. All the commercial carbons displayed % attrition values below 10%, which only one of the nutshell-based carbons was below 10% attrition. The % attrition observed in carbons is the result of the density or hardness of the starting material.

Acid-activated pecan shell carbon, PSA showed the lowest attrition (7.1 %) among experimental carbons, followed by physically-activated pecan shell-based carbons such as carbon dioxide-activated pecan shell-based carbon, PSC (12.79 %), steam-activate pecan shell-based carbon, PSS (22.15 %) and acid-activated almond shell based carbon ALA (31.68 %). Acid-activated almond shell-based carbon, ALA showed the highest attrition value thereby making it undesirable because of its susceptibility to abrasion losses during commercial utilization. Among the experimental carbons only acid-activated pecan shell-based carbon, PSA (7.10 %) was not significantly (5% significance) different from coconut shell-based commercial activated carbons such as GRC-20 (7.27 %) and 206C AW (7.26 %). The other experimental carbons (ALA, PSC, and PSS) were significantly (5% significance) different from all the commercial carbons (F200, GRC-20, and 206C AW).

Since pecan shells have higher density than almond shells, almond shell carbons would be softer with higher attrition values, which was the case in this study. The

surface area appeared to have little effect on attrition for both the commercial and experimental samples.

3.4.2 Chemical Properties of GACs

The chemical properties (ash, pH and conductivity) of the granular activated carbons are presented in Table 3.2.

Ash Content: Ash content is a measure of the minerals as impurities in the carbons mainly derived from the carbon precursor. Ash content of Calgon's coconut shell-based carbon (GRC-20) had the highest ash content (9.6%) when compared to Filtrasorb 200 (F200) and Waterlinks coconut shell-based carbon of 6.5% and 2.00% respectively. Among experimental carbons carbon dioxide-activated pecan shell-based carbon (PSC) had highest ash content 6.00% followed steam-activated pecan shell-based carbon (PSS) with 5.53%, acid-activated almond shell-based carbon (ALA) with 3.35%, acid-activated pecan shell-based activated carbon with (PSA), 1.42%. Acid-activated pecan shell based carbon (PSA) had the lowest ash content making it most desirable carbons of all the carbons analyzed for this study followed by Waterlinks coconut shell-based carbon.

Acid-activated experimental carbons (ALA, PSA) had lower ash content when compared to physically activated carbons. Statistical analysis showed that all-experimental carbons (ALA, PSA, PSC, and PSS) to be significantly different from commercial carbons (F200, GRC-20, and 206C AW).

pH: pH of the carbon directly impacts the adsorption process and affects the final pH of the treated municipal wastewater. Therefore a neutral pH is generally preferred.

Table 3.1: Physical properties of experimental and commercial granular activated carbons.

Physical Properties	Experimental Carbons				Commercial Carbons		
	Chemical activation		Physical activation		F200	GRC-20	206C AW
	ALA	PSA	PSC	PSS			
Surface area (m^2/g)	1340^{abc}	902^{ab}	435^{abc}	917^{ab}	835	1038	898
Bulk density (g/m^3)	0.30 ($\pm$0.005)^{abc}	0.51 ($\pm$0.003)^{abc}	0.57 ($\pm$0.002)^{abc}	0.49 ($\pm$0.001)^{bc}	0.49 ($\pm$0.005)	0.47 ($\pm$0.004)	0.54 ($\pm$0.001)
Attrition (%)	31.68 ($\pm$1.05)^{abc}	7.10 ($\pm$0.45)^{ad}	12.79 ($\pm$0.11)^{abc}	22.15 ($\pm$0.96)^{abc}	3.26 ($\pm$0.07)	7.27 ($\pm$0.96)^{d}	7.26 ($\pm$1.21)^{d}

Commercial carbons
F200: Filtrasorb 200.
GRC-20: Coconut shell-based activated carbon (Calgon Carbon Corporation).
206C AW: Coconut shell-based activated carbon (Waterlinks).

Experimental carbons
ALA: Almond shell-based acid-activated carbon.
PSC: Pecan shell-based carbon dioxide-activated carbon.
PSS: Pecan shell-based steam-activated carbon.
PSA: Pecan shell-based acid-activated carbon.

[a] Significantly different from Filtrasorb 200 (F-200) at 5% significance level.
[b] Significantly different from Calgon coconut shell-based GAC (GRC-200) at 5% significance level.
[c] Significantly different from Waterlinks coconut shell-based GAC (206C AW) at 5% significance level.
[d] Standard deviation of the means significantly different at 5% significance level.

The pHs of the commercial carbons (F200, GRC-20, and 206C AW) were 7.4, 8.63, and 8.15 respectively. The pH of the experimental carbons mainly depended on the activation process. Acid-activated carbons such as almond shell-based carbon (ALA) and pecan shell-based carbon (PSA) had acidic pH (6.08 and5.70, respectively) and physically activated experimental carbons such as carbon dioxide-activated pecan shell-based carbon and steam-activated pecan shell-based carbon (PSS) had basic pH (10.07 and 10.01, respectively). Statistical analysis showed that all the experimental carbons were significantly different (5% significance) from the commercial carbons.

Conductivity: High conductivity of the carbons is undesirable as it interferes in the adsorption process because of the leachable minerals associated to the carbon surface.

Filtrasorb 200 (F200) had the lowest conductivity of 5.85 µS, followed by Calgon's coconut shell-based GRC-20 (9.08 µS) and Waterlinks coconut based 206C AW (11.95 µS). Physically activated experimental carbons (PSC and PSS) had high conductivity values consisting of 330.66 µS and 752.76 µS, respectively. Chemically activated experimental carbons (ALA and PSA) showed lower conductivity than the physically activated carbons, with conductivity values of 27.11 µS and 46.03 µS, respectively. Conductivity of all the experimental carbons was significantly (5% significance) higher than the commercial activated carbons.

Statistical Analysis

The statistical analysis based on non-hierarchical clustering is presented in Table 3.3. Steam-activated and acid-activated pecan shell-based activated carbons (PSS and PSA) grouped with the commercial carbons (cluster 1) whereas carbon dioxide- activated pecan shell-based carbon (PSC) and acid-activated almond shell-based carbon

Table 3.2: Chemical properties of experimental and commercial granular activated carbons.

Chemical Properties	Experimental Carbons				Commercial Carbons		
	Chemical activation		Physical activation				
	ALA	PSA	PSC	PSS	F200	GRC-20	206C AW
Ash (%)	3.35 ($\pm$0.02)[abc]	1.42 ($\pm$0.01)[abc]	6.00 ($\pm$0.08)[abc]	5.53 ($\pm$0.20)[abc]	6.57 ($\pm$0.03)	9.60 ($\pm$0.07)	2.00 ($\pm$0.07)
PH	6.08 ($\pm$0.41)[abcd]	5.70 ($\pm$0.52)[abcd]	10.07 ($\pm$0.04)[abc]	10.01 ($\pm$0.16)[abc]	7.4 ($\pm$0.78)	8.63 ($\pm$0.78)	8.15 ($\pm$0.06)
Conductivity (μm)	27.11 ($\pm$1.82)[abcd]	46.03 ($\pm$0.29)[abc]	330.96 ($\pm$0.77)[abc]	752.76 ($\pm$3.40)[abc]	5.85 ($\pm$0.35)[d]	9.08 ($\pm$0.77)[d]	11.95 ($\pm$0.13)

Commercial carbons
F200: Filtrasorb 200.
GRC-20: Coconut shell-based activated carbon (Calgon Carbon Corporation).
206C AW: Coconut shell-based activated carbon (Waterlinks).

Experimental carbons
ALA: Almond shell-based acid-activated carbon.
PSC: Pecan shell-based carbon dioxide-activated carbon.
PSS: Pecan shell-based steam-activated carbon.
PSA: Pecan shell-based acid-activated carbon.

[a] Significantly different from Filtrasorb 200 (F-200) at 5% significance level.
[b] Significantly different from Calgon coconut shell-based GAC (GRC-200) at 5% significance level.
[c] Significantly different from Waterlinks coconut shell-based GAC (206C AW) at 5% significance level.
[d] Standard deviation of the means significantly different at 5% significance level.

(ALA) grouped in cluster 2 and cluster 3 respectively. Acid-activated experimental carbons (Pecan shell-based (PSA) as well as almond shell-based (ALA)) grouped closely with commercial carbons (F-200, GRC-20, and 206C AW) with respect to chemical and overall properties. Acid-activated pecan shell-based carbons (PSA) grouped with the commercial carbons (F200, GRC-20, and 206C AW) in all the parameters analyzed thus emphasizing its closeness to the commercial carbons. It is noteworthy that all commercial carbons grouped together in all the three parameters studied.

Table 3.3: Non-hierarchical clustering of GACs based on their physical, chemical and overall properties.

	Cluster 1	Cluster 2	Cluster 3
Physical properties	F200 GRC-20 206C AW PSS PSA	PSC	ALA
Chemical properties	PSS	F200 GRC-20 206C AW ALA PSA	PSC
Overall properties	PSS	PSC	F200 GRC-20 206C AW ALA PSA

Commercial carbons: F200: Filtrasorb 200; GRC-20: Coconut shell-based activated carbon (Calgon Carbon Corporation); 206C AW: Coconut shell-based activated carbon (Waterlinks).

Experimental carbons: ALA: Almond shell-based acid-activated carbon; PSC: Pecan shell-based carbon dioxide-activated carbon; PSS: Pecan shell-based steam-activated carbon; PSA: Pecan shell-based acid-activated carbon.

Principal Component Analysis (PCA) in Figure 3.1 shows that acid-activated pecan shell and acid-activated almond shell-based granular activated carbons (PSA and ALA) grouped in the same quadrant as Filtrasorb 200 and Waterlinks coconut shell-based granular activated carbons (F-200 and 206C AW, respectively). Calgon based coconut

shell carbon (GRC-20); physically activated pecan shell based granular activated carbons (PSC an PSS) occupied separate quadrants respectively.
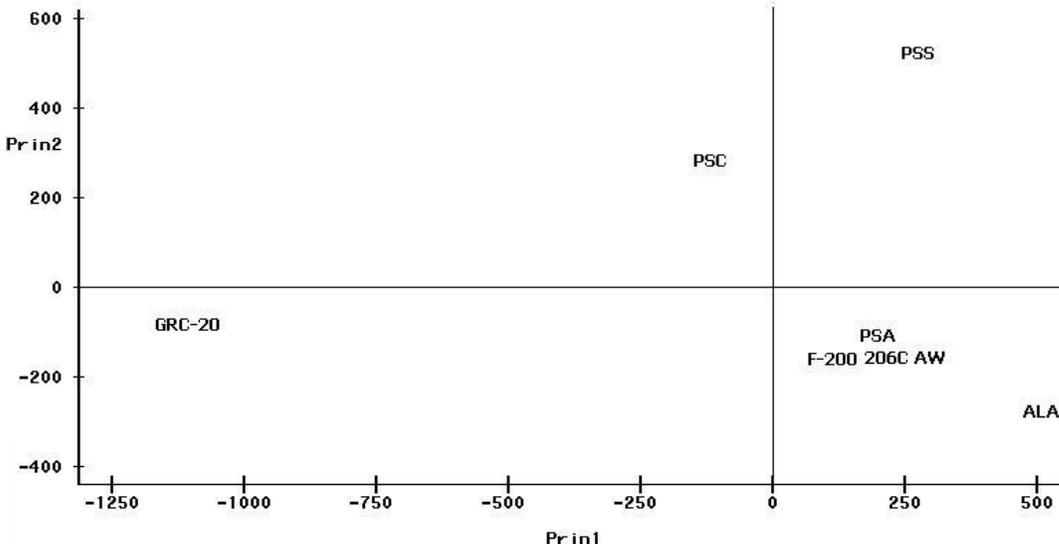
Figure 3.1: Principal component analysis on combined physical and chemical properties of experimental and commercial granular activated carbons (GACs)

Commercial carbons: F-200: Filtrasorb 200; GRC-20: Coconut shell-based activated carbon (Calgon Carbon Corporation); 206C AW: Coconut shell-based activated carbon (Waterlinks).

Experimental carbons: ALA: Almond shell-based acid-activated carbon; PSC: Pecan shell-based carbon dioxide-activated carbon; PSS: Pecan shell-based steam-activated carbon; PSA: Pecan shell-based acid-activated carbon.

3.5 Conclusions

Among the shell-based experimental carbons, almond shell-based chemically activated granular activated carbon (ALA) had the largest total surface area with 1340 m^2/g, followed by steam-activated pecan shell-based carbon with 917 m^2/g, acid-activate pecan shell-based carbon 902 m^2/g and carbon dioxide-activated pecan shell-based carbon 435 m^2/g. Comparison of the total surface area of the pecan and almond shell-based experimental carbons to the total surface area of the commercial carbons showed that almond shell-based chemically activated carbon had significantly (5% significance)

larger surface than F200 (Filtrasorb 200), GRC-20 (Calgon coconut based carbon), and 206C AW (Waterlinks coconut shell-based carbon).

Experimental and commercial carbons indicated that the bulk density of the ALA, experimental carbon was significantly (5% significance) greater than F200, GRC-20, and 206C AW. However, with in the pecan shells-based, physical activation by carbon dioxide had significant (5% significance) positive affect on the bulk density compared to chemical activation by acid as reflected by the data, that the bulk density of the carbon PSC to be 0.57 g/m^3 compared to that of PSA equal to 0.51 g/m^3. The overall bulk density result indicate that pecan shell-based granular activated carbon were comparable to the commercial carbons.

The lowest attrition in the commercial carbons (F200) was bituminous coal based carbon. Acid-activated pecan shell carbon, PSA showed the lowest attrition (7.1 %) among experimental carbons, followed by physically activated pecan shell carbons such as carbon dioxide-activated pecan shell-based carbon, PSC (12.79 %), steam-activate pecan shell-based carbon, PSS (22.15 %) and acid-activated almond shell-based carbon ALA (31.68 %). Among the experimental carbons, only acid-activated pecan shell-based carbon, PSA (7.10 %) was not significantly (5% significance) different from coconut shell-based commercial activated carbons such as GRC-20 (7.27 %) and 206C AW (7.26 %).

Among experimental carbons carbon dioxide-activated pecan shell-based carbon had highest ash content of 6.00% followed by steam-activated pecan shell-based carbon (PSS) with 5.53%, acid-activated almond shell-based carbon (ALA) with 3.35%, acid-activated pecan shell-based carbon, (PSC) with 1.42%. Acid-activated pecan shell-based

carbon (PSA) had the lowest ash content making it most desirable carbons of all the carbons analyzed for this study followed by Waterlinks coconut shell-based carbon (GRC-20).

Acid-activated experimental carbons (ALA, and PSA) had lower ash content when compared to physically activated carbons (PSS, and PSC). Acid-activated carbons such as almond shell-based carbon (ALA) and pecan shell-based carbon (PSA) had acidic pH, 6.08 and 5.70, respectively and physically activated experimental carbons such as carbon dioxide-activated pecan shell-based carbon and steam-activated pecan shell-based carbon (PSS) had basic pH, 10.07 and 10.01, respectively. Statistical analysis showed that all the experimental carbons were significantly different (5% significance) from the commercial carbons.

Chemically activated experimental carbons (ALA and PSA) showed lower conductivity than the physically activated carbons, with conductivity values of 27.11 μS and 46.03 μS, respectively. Conductivity of all the experimental carbons was significantly (5% significance) higher than the commercially activated carbons.

Cluster analysis resulted in steam-activated and acid-activated pecan shell-based activated carbons (PSS and PSA) grouping with the commercial carbons (cluster 1) whereas carbon dioxide-activated pecan shell-based carbon (PSC) and acid-activated almond shell-based carbon (ALA) grouped in cluster 2 and cluster 3 respectively. Principal component analysis results indicated that acid activated pecan shell-based carbon (PSA) grouped with the commercial carbons (F200, GRC-20, and 206C AW) in all the parameters analyzed thus emphasizing its closeness to the commercial carbons.

Calgon's based coconut shell-based carbon (GRC-20), physically activated pecan shell based granular activated carbons (PSC an PSS) occupied separate quadrants respectively.

CHAPTER 4
PECAN AND ALMOND SHELL-BASED GRANULAR ACTIVATED CARBONS (GACs) FOR TREATMENT OF ORGANIC CONTAMINANTS IN MUNICIPAL WASTEWATER

4.1 Introduction

Activated carbon, carbon that is treated by high temperature heating with steam or carbon dioxide producing an internal porous particle structure, has been used for many years in industrial processing, in wastewater treatment. Activated carbons can be divided in to two main classes, those used for adsorption of gases and vapors for which a granular activated material is usually employed, and those in purification of liquids for which a powdered material is desired. Granular activated carbons (GACs) are used in the form of a bed in the water treatment. The wastewater flows through the bed, where organic molecules present as contaminants are attracted by the carbon and adsorbed on its surface. When the carbon is saturated with the adsorbed molecules, the carbon loses its adsorptive ability; it is removed from the system and regenerated.

Many carbonaceous materials, such as petroleum coke, sawdust, lignite, coal, peat, wood, charcoal, nutshell, and fruit pits may be used for the manufacture of activated carbon, but the properties of the finished material are governed not only by the raw material, but also by the method of activation used. The choices of the raw material are based upon the end use of the activated carbon, availability, cost of the raw material, and national and international economic and political atmosphere. For instance, decolorizing activated carbons are usually employed as powders. The raw materials for the powdered carbon are either structure less or have weak structure, such as rice straw, sugarcane bagasse, soybean hull, sawdust, and peanut shells. Vapor adsorbent carbons are used in the form of hard granules; and generally granular activated carbons (GACs) are made in the United States, and are derived from a non-renewable resource, namely coal, and therefore competes with the energy industry for this diminishing commodity.

Abundance and low cost of agriculture by-products make them good candidates as precursors of activated carbons. It has been shown by Ng, (2001) that by-product based activated carbons cost half as much as coal based carbons and in some instances even surpasses the adsorption efficiency of coal based carbons.

The annual harvesting and processing of various agricultural crops grown in the United States yield considerable quantities of agricultural by-products. Paying attention to by-products, which have been shown to have potential as raw materials in the manufacture of activated carbons (Toles et al., (1997), (1998), (1999); Johns et al., (1998)). The United States produced 93 billion lbs of sugarcane, 21 billion lbs of rough rice, 315 million lbs of pecan, and 850 million lbs almonds for year 2001 (Agricultural Statistics, 2002). Production and processing of these commodities is estimated to generate 32 billion lbs of sugarcane bagasse, 4.7 billion lbs of rice hulls/straw, and 157 million lbs of pecan shells, and 425 million lbs of almond shells, as by-products per year. Some of the commodities, such as sugarcane, rice, and pecans, which produce these by-products, are of economic importance also to Louisiana agriculture.

In recent years, there has been an increasing awareness of the limited water resource currently available. This recognition has led to the concept of water reuse rather than disposal. Acceptance of the concept of reuse has been accelerated by the development of new wastewater treatment processes that can yield high effluents at economically feasible levels. One such is the adsorption process by activated carbon treatment.

A comprehensive review of literature has shown that there is an urgent need in wastewater treatment plants to find economically affordable alternate carbonaceous adsorbents to the currently used commercial carbons which are getting more expensive and running in short supply, especially the ones which have to be imported. Therefore, the present investigation was

undertaken (1) to compare the adsorption efficiency of pecan shell-based carbons with respect to COD (a measure of the oxygen required to degrade the organic material present in wastewater) and (2) to determine the effectiveness of using pecan and almond shell-based GACs in the adsorption of volatile organic matter (VOC) (compounds of health concern and known toxic compounds such as bromo-dichloromethane, benzene, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, and 1,1 dichloroethane) to the adsorption efficiency of commercially used carbons such as Filtrasorb 200, Calgon GRC-20, and Waterlinks 206C AW) in a simulated test medium.

4.2 Materials

4.2.1 Experimental and Commercial GACs

Seven activated carbons consisting of four experimental carbons, namely (i) Pecan shell-based steam-activated (ii) Pecan shell-based carbon dioxide-activated (iii) Pecan shell-based acid-activated (iv) Almond shell-based acid-activated were produced at USDA, Southern Regional Research Center, New Orleans, LA, and were furnished for analysis and three commercial carbons, namely (v) Filtrasorb-200 (vi) Calgon (Pittsburgh, PA) coconut shell-based activated carbon (GRC-20) and (vii) Waterlinks (Barneby Sutcliffe, Ohio) coconut shell-based activated carbon (206C AW) were selected for this experiment. The COD test vials were procured from HACH (Loveland, CO). The volatile organic compounds mix was procured from Supelco (Bellefonte, PA).

4.2.2 Collection of Municipal Wastewater Samples

Primary treated municipal wastewater was collected from the Central Municipal Processing Plant at Baton Rouge, LA. The wastewater was filtered using Whatman #4 filter paper to remove suspended particles and used immediately after filtration.

4.3 Methods

4.3.1 Chemical Oxygen Demand (COD)

The granular activated carbons were powdered to reduce the particle size to < 325 mesh (45 μm) as this would eliminate particle size as the rate limiting step for adsorption (Randtke et al., 1983). Different carbon dosages ranging from 0.01 to 1.5 g per 100 ml of wastewater were used for this study. Adsorption was carried out for 2 h. After adsorption the samples were filtered using 0.45 μm PTFE filter and the filtered samples were stored at 4ºC until analyzed for residual COD levels.

The COD of the experimental and commercial activated carbons, treated and untreated (control) samples were determined by colorimetric method (5220D) recommended by Standard Method for Examination of Water and Wastewater (Clesceri et. al., 1998). The test method consisted of the use of HACH (Loveland, CO) test vials, containing dichromate reagent as a chemical oxidant for measuring COD in the range of 0-1500mg/L.

4.3.2 Volatile Organic Adsorption

The six organic compounds selected to test the adsorption effectiveness of the experimental and commercial GACs included 1,1 dichloroethane, chloroform, benzene, 1,1,1-trichloroethane, carbon tetrachloride and bromo-dichloromethane. They were chosen, because of their known occurrence in municipal wastewater and proven to be toxic and hazardous to health under EPA listed toxic water pollutants potentially available in petroleum refinery wastewater (Liu and Liptak, 2000). Furthermore, these organic compounds represent a wide range of polarities and activated carbons have been shown to have varying affinity to compounds with varying polarity.

The method developed and used in this study utilizes 0.01 g carbon in contact with a solution containing100 ppb each of the six analyte listed above. Forty milligrams of the carbons

were added to environmental sample vials and 40 ml of distilled deionized water was added and spiked with 40 μl of the stock solution containing 50 ppm of each analyte to get a final concentration of 100 ppb of each analyte in the test medium for the adsorption experiment. The samples were run in triplicates along with blanks, concurrently with the samples. The carbons were left in contact with the analytes for 24 h at room temperature with constant agitation at 500 rpm. After the contact time, an aliquot of the solution (15 ml) was drawn off and preserved in an environmental sample vials under refrigeration temperature until analyzed by gas chromatography for residual organics in the samples.

The vials containing 15 ml of the above mentioned carbon treated solution was used as headspace sampling by Micro-Fast gas chromatography with FID detector and 1.2 m DB-170 column with 0.4 Fm film thickness and 0.1 mm i.d. Hydrogen was used as carrier gas and the sorption trap consisted of 5 mg tenax GR with 80/100-mesh size. Injection time was set to 1000 msec and desorption temperature was adjusted to 250EC. The column temperature was ramped from 30EC to 180EC at 5EC/sec. Calibration curve was constructed by using standard solution with 25 ppb, 50ppb and 100 ppb with r >0.95 for each analyte.

Statistical Analysis

Multivariate technique such as Principal Component Analysis (PCA) and cluster analysis were carried out to interpret the data in order to group the carbons based on their physical and chemical properties, adsorptive properties, and overall properties. Principal component analysis (SAS, 1989) uses a scatter plot with four quadrants along the x and y-axis. The distribution of carbons based on their overall adsorptive properties was studied. For cluster analysis (SAS, 1989) both hierarchical and non-hierarchical techniques were analyzed.

4.4 Results and Discussion

4.4.1 Adsorption of Chemical Oxygen Demand (COD)

Effect of Carbon Dosage on COD Adsorption of Test Solution

The effects of carbon dosage (g/100ml) ranging from 0.0 to 1.5 and the three experimental (PSA, PSC, and PSS) and one commercial (F200) carbon on the COD adsorption of the test solution are presented in Figure 4.1. The initial COD concentration of the untreated municipal wastewater ranged from 40.0 mg/l to 66.5 mg/l and the corresponding pH was 7.55.

An analysis of the graphs presented in Figure 4.1 indicate that the pecan shell steam activated and pecan shell-based acid-activated carbons had higher adsorptive capacities with respect to COD adsorption than the pecan shell-based carbon dioxide-activated carbon and Filtrasorb 200. This was true throughout the range of the carbon dosages used. The adsorption performance of the control (F200) with respect to COD was higher than pecan shell-based carbon dioxide-activated carbon but lower than pecan shell-acid activated and pecan shell-based steam-activated carbon. A comparison of the performance efficiency of steam- and acid-activated carbons indicates that between 0.00 to 0.6 mg/100ml carbon dosages, acid-activated pecan shell-based carbon did better than steam-activated carbon. However, beyond 0.6 up to 1.5 range, the performance of these two carbons remained almost equal.

An analysis of these observations indicates that, (1) with respect to adsorption of COD by pecan shell-based activated carbon, steam-activation appears to bring a more desirable effect than carbon dioxide-activation although these two activation methods are physical; (2) The pecan shell-based activated carbons (PSA, and PSS) are better adsorbents with respect to COD than Filtrasorb 200, a bituminous coal-based carbon and; (3) confirms the established hypothesis that surface area affects adsorption positively.

Application of Freundlich Model to COD Adsorption

Adsorption isotherms expressed as Freundlich isotherm constants have been found to be better measure of the adsorptive properties of the activated carbons and is based on the distribution of COD between the activated carbon and aqueous phases at equilibrium. The basic Freundlich equation is:

$$x/m = kc^{1/n} \qquad \text{(Eq. 1)}$$

where,

x = amount of COD adsorbed

m = weight of carbon

x/m = concentration of COD adsorbed

c = equilibrium concentration of COD in solution

k and n are constants

A linear form of the Freundlich equation is represented by:

$$\log(x/m) = \log k + 1/n \log c$$

The data on the effects of carbon dosage and three experimental and one commercial carbon on the COD adsorption of the test medium was fitted to a Freundlich model and a graphical representation of this model showing the adsorption isotherms of pecan shell-based carbons activated and control carbons on COD is presented in Figure 4.3. The respective constants k and $1/n$ are presented in Table 4.1. The representation of the experimental data by Freundlich equation resulted in a linear curve with $r > 0.95$. In Figure 4.3, the log x/m values represent the relative adsorption efficiency of the activated carbons and Ce, the residual concentration of the organic solutes in the treated test solution. From Figure 4.3, it appears that acid and steam activated pecan shell-based activated carbon with higher log x/m ratio

49
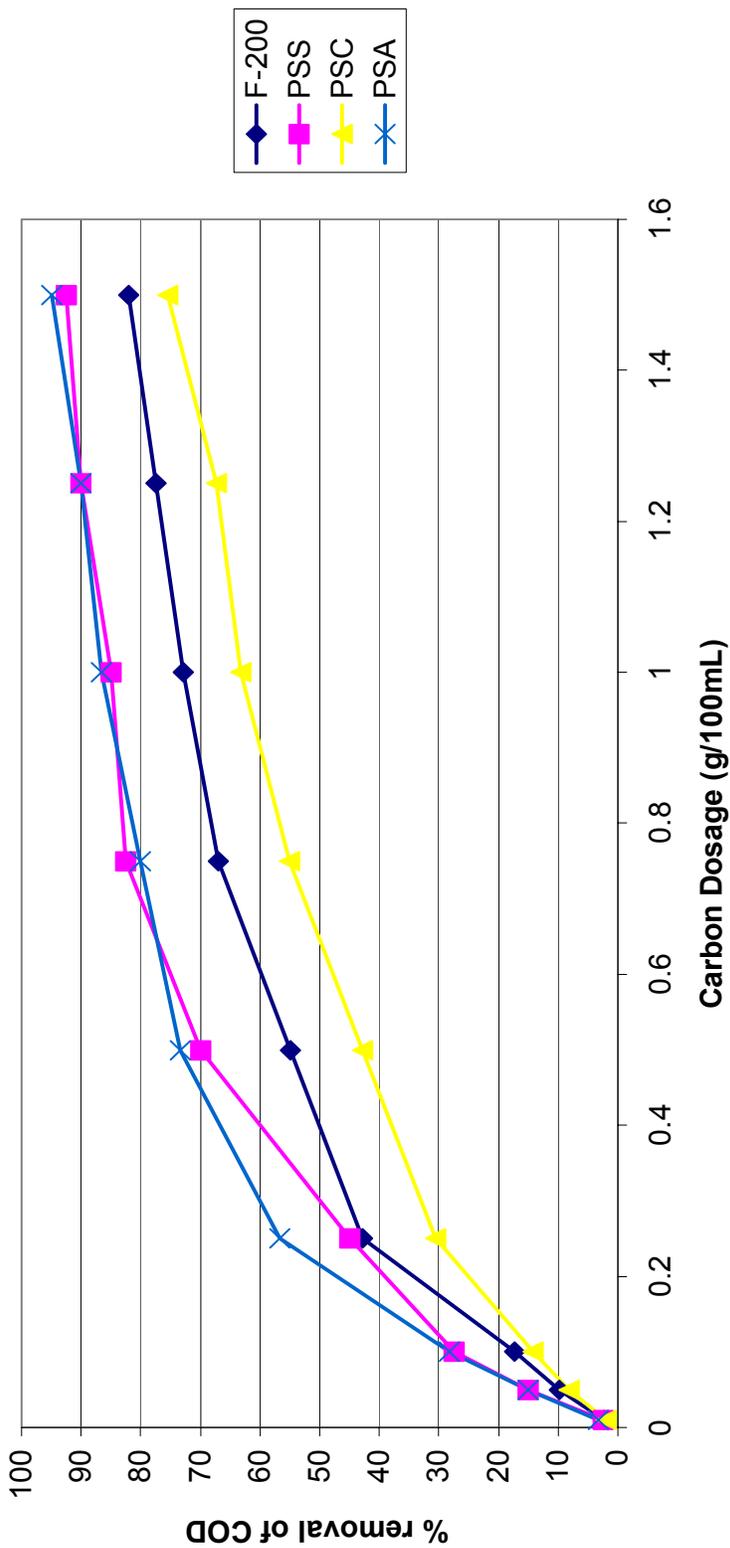
Figure 4.1 Percentage removal of COD by experimental and commercial powdered activated carbons.
Average Initial concentration of COD: 53.25 mg/L

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

50

Figure 4.2 Effect of carbon dosage on the change in pH of the treated wastewater.
Average Initial concentration of COD: 53.25 mg/L

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

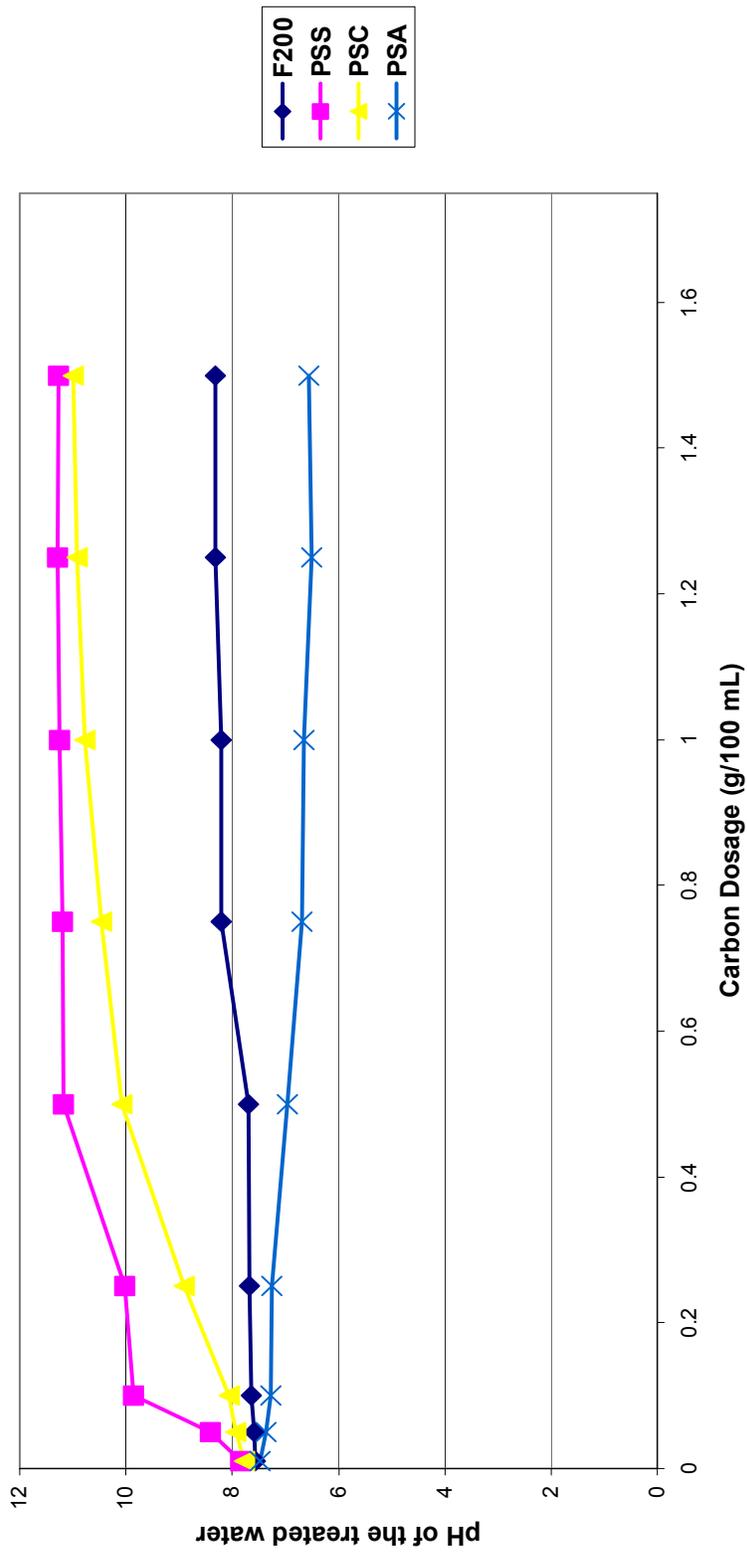had better adsorption efficiency than the commercial and carbon dioxide-activated pecan shell-based carbon. This observation was found to be true throughout the carbon dosage range used in this study (0.0 to 1.5 g/100ml). The linear curve for acid-activated pecan shell-based carbon and steam-activated pecan shell-based carbon was spread over a broader range of log Ce (from 0.4 to 1.8) whereas, the increase in the log x/m values of carbon dioxide-activated and commercial carbons was with in a narrow range of log Ce values (from 1.2 to 1.8). These results appear to infer that in terms of the adsorption efficiency, (1) chemical activation of the pecan shells produces more efficient carbon compared to physical activation; (2) commercial F200, a bituminous coal-based carbon was better in adsorption efficiency than pecan shell-based carbon dioxide-activated carbon, but not as good as the acid- and steam-activated pecan shell-based carbons.

In Table 4.1, is presented the k and 1/n values for experimental and commercial carbons. k and 1/n represent the intercept and slope of the adsorption isotherms in Figure 4.3.

Higher the k value larger the adsorption efficiency of the activated carbon. A larger value for 1/n indicates a larger change in effectiveness over different equilibrium concentrations. Also, when 1/n is greater than 1.0 the change in adsorbed concentration is greater than the change in the solute concentration. Once the coefficients k and 1/n have been determined, x and m can be calculated for all concentrations (Eq. 1).

Generally a carbon that has a higher x/m value at a specified equilibrium concentration will be preferred for a given application (US Environmental Protection Agency, 1973). In this investigation, the pecan shell-based acid-activated carbon (PSA) had the highest k value (15.8197) followed by pecan shell-based steam-activated

(12.4422), pecan shell-based carbon dioxide-activated carbon (1.7414) and commercial carbon Filtrasorb 200 (4.7043). Based on k values only the adsorption effectiveness of PSA was nearly four times that of the commercial carbon, more than 12 times that of PSC and 30 % more than PSS for the carbon dosages used in this study. Other process variables being independent, the preceding data appear to infer that chemical activation increases the k values thereby the adsorption efficiency.

Among the three experimental carbons (PSA, PSS and PSC) and one commercial carbon (F200), PSC had the highest $1/n$ value (1.0020) followed by F200 (0.8166), PSA (0.6212) and PSS (0.6094). These values of $1/n$ corresponding to the respective carbons indicate that PSC has the highest rate of adsorption of the solute and PSS the least. These values of $1/n$ for PSC and PSS also suggest that with in the physical activation carbon dioxide-activation of pecan shells improves $1/n$ compared to steam-activation of the pecan shells-based carbons. Furthermore, PSC with $1/n > 1.0$ (1.0020) indicates that the change in adsorbed solute (organic contaminants) concentration is greater than the change in the solute concentration. The r values (Table 4.1) of all four activated carbons are greater than 0.95 indicating that the graphs on Figure 4.3 are linear and valid within the carbon dosage used.

Effects of Carbon Dosage on pH of the Test Solution

The effect of carbon dosage (g/100ml) ranging from 0.0 to 1.5 g/100 ml for the three experimental (PSA, PSC, PSS) and one commercial (F200) carbon on the pH of the test solution is presented in Figure 4.2. The average initial pH of the untreated municipal wastewater was 7.55. Data presented in Figure 4.2 show that the pH of the test solution did not change on treatment with Filtrasorb 200, a bituminous coal-based carbon. The

acid-activated pecan shell-based carbon did affect the pH of the solution lowering it to a little above 6.0 at 1.5 g/100 ml carbon dosages. This observation appears rational in that the acidity from the acid activated carbon has contributed in lowering the pH of the test solution. However, the effect of carbon dioxide- and steam-activated carbon on the pH of the test solution was completely opposite in that they increased the pH of the test medium making it more alkaline. The increase was from 7.5 at 0.0 g/100ml carbon dosage to almost 11.0 at 1.5 g/100 ml carbon dosage.

The preceding results appear to infer that, within the carbon dosage used in this study, (1) that the commercial bituminous coal-based carbon did not have either positive or negative effect on the pH of the test solution. However, the experimental pecan shell-based carbons did have either negative or positive effects on the pH of the test solution. The nature of the effect depended on whether the pecan shell-based was activated either physically or chemically. (2) that within the two physical methods of activation, namely by steam- or carbon dioxide-, steam-activated carbon increased the pH of the test solution more than the increase in the pH contributed by carbon dioxide-activated carbon. Therefore, it appears that the selection of a specific method of physical activation is a factor which should not be overlooked in the preparation of specified granular activated carbons, and (3) that the actual change in pH caused by both the experimental carbons and the commercial carbon was pronounced within the carbon dosage range of 0.0 to 0.5 g/100 ml. Increase in the carbon dosage beyond 0.5 g/100ml up to 1.5 g/100ml, did not have appreciable effect on the pH. In other words, the pH of the solution treated by all the carbons, regardless of the raw materials used, and remained almost the same at carbon dosage ranging from 0.5 to 1.5 g/100ml.

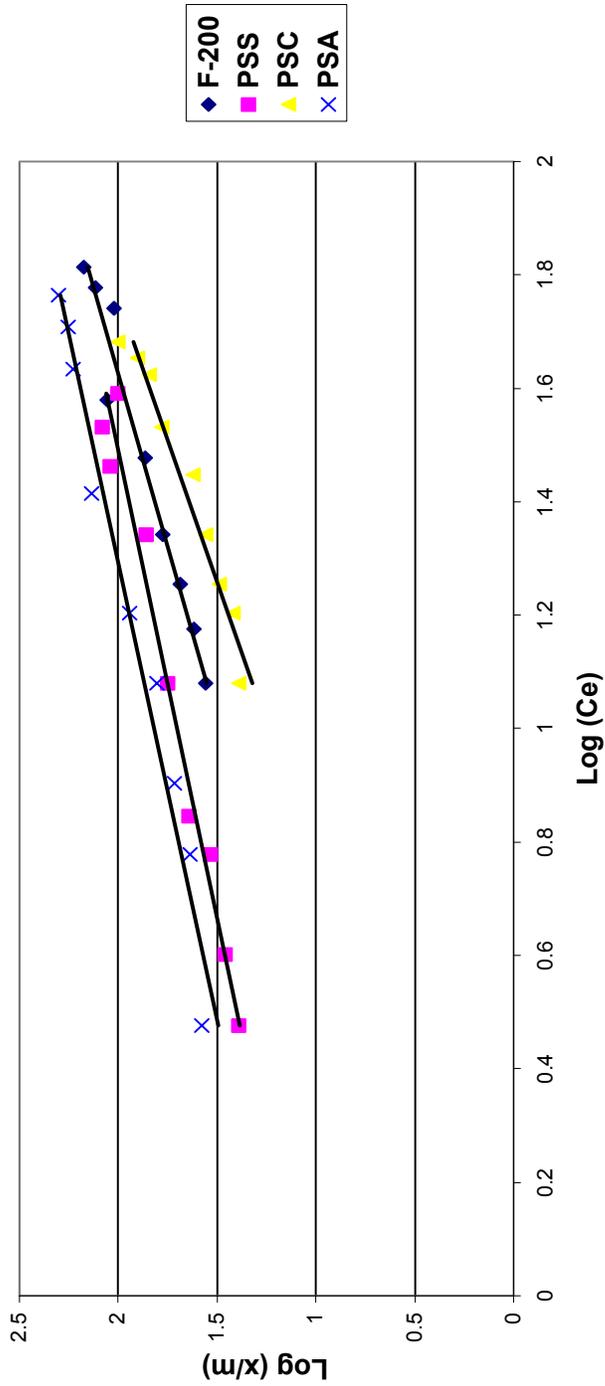**Figure 4.3** Adsorption isotherms of pecan shell-based and commercial activated carbon on Chemical Oxygen Demand (COD).

Average Initial concentration of COD: 53.25 mg/L

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

55

Table 4.1: Freundlich constants for COD adsorption isotherms

GAC	k	1/n	r	α
PSA	15.8197	0.6212	0.9708	<0.05
PSS	12.4422	0.6094	0.9713	<0.05
PSC	1.7414	1.0020	0.9562	<0.05
F200	4.7043	0.8166	0.9625	<0.05

Experimental GAC
Physical activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated
Chemically activated GAC
PSA- Pecan shell acid-activated

Commercial GAC
F200- Filtrasorb 200 (Bituminous coal based)
n and k are dimensionless constants of Freundlich model; r: linear correlation coefficient, α: Type I error.

4.4. 2 Adsorption of Volatile Organic Compounds (VOCs)

In Figure 4.4 and Table 4.2 is presented the data on the adsorption of volatile organic compounds consisting of one aromatic compound (benzene) and five halogenated aliphatic compounds (bromo-dichloromethane, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, and 1,1 dichloroethane) by four experimental carbons (pecan shell carbon dioxide-activated-PSC, pecans shell steam-activated-PSS, pecan shell acid-activated-PSA, and almond shell acid-activated-ALA) and three commercial carbons (Filtrasorb 200-F200, bituminous coal-based; Calgon GRC-20, coconut shell-based; and Waterlinks 206C AW, coconut shell-based). The experimental carbon ALA and two commercial carbons GRC-20 and 206C AW, which were not a part of the previous study, were included in this study because the commercial samples were furnished gratis by the manufacturers and USDA supplied the ALA samples.

The data from Figure 4.3 indicates that in terms of adsorption of composite organic compounds in the test medium, 206C AW showed the highest performance (516.06 ppb) followed by PSS (506.06 ppb), GRC-20 (502.32 ppb), F200 (476.57 ppb), PSC (426.96 ppb), PSA (407.37 ppb) and ALA (347.30 ppb). From the adsorption data from Figure 4.3, It appears that within the three commercial carbons, 206C AW and GRC-20, coconut shell-based carbons, exceeded F200 a bituminous coal-based carbon, in adsorption of composite organic compounds in the test medium. Among the four experimental carbons, the three-pecan shell-based carbons PSA, PSS and PSC exceeded ALA in their adsorption performance. The physically activated pecan shell-based carbons (steam and carbon dioxide) were superior in their adsorption to chemically activated pecan as well as almond shell-based carbons, this could be due to the inhibition of small organics from penetrating into the micropores due to the presence of greater number of polar compounds on the mesopore and macropore surface of the acid activated carbons. These data infer that the method of activation and precursors selected for the preparation of activated carbons do effect the adsorption of volatile organic compounds and hence are factors to be considered in any adsorption process. All the carbons studied exhibited efficient adsorbability of benzene possibly because of its zero dipole moment. Acid-activated experimental carbons showed activated adsorption (93.14%) of 1,1,1-trichloroethane all the carbons studied.   Steam-activated pecan shell-based carbon showed higher adsorptive capacity (85.45%) of bromo-dichloromethane against all the carbons studied. It can be inferred that the adsorption of the VOCs mainly depends not only on the carbon precursor but also on the method of activation, which influence the surface chemistry of the carbons.
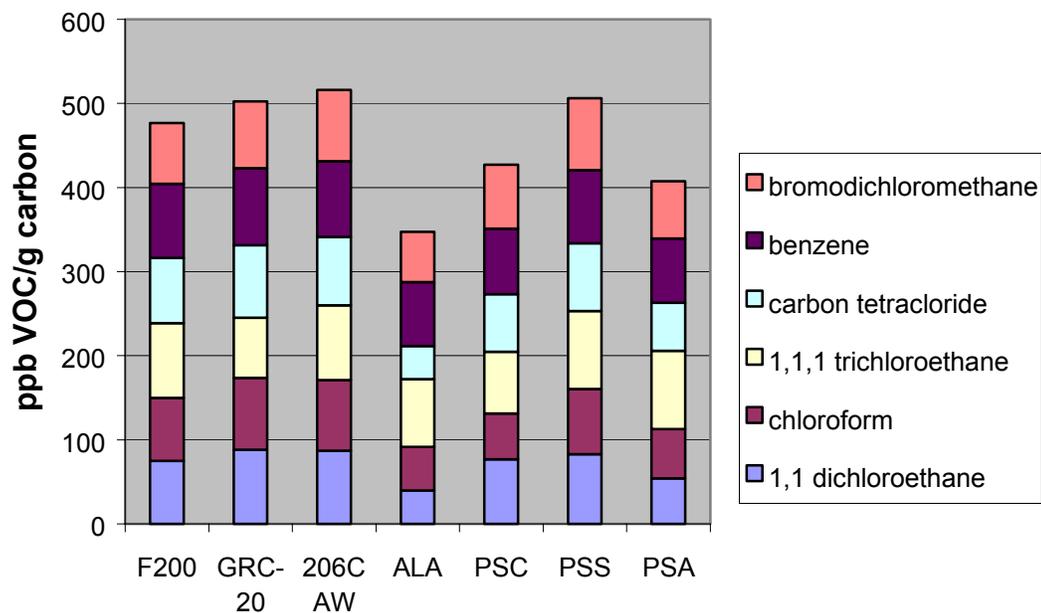
Figure 4.4: Composite adsorption of VOCs by experimental and commercial GACs.

Commercial GAC
Bituminous Coal GAC
F200- Filtrasorb 200 (Bituminous coal based)

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Coconut based GAC
GRC-20- Calgon coconut shell based
206C AW-Waterlinks coconut shell based

Chemically activated GAC
PSA- Pecan shell acid-activated
ALA- Almond based acid-activated

Table 4.2: Individual adsorption of volatile organic compounds (%) by experimental and commercial GACs.

	bromo dichloromethane	benzene	carbon tetracloride	1,1,1 trichloro ethane	chloroform	1,1 dichloro ethane
F200	72	88.32	77.5	88.9	74.89	74.96
GRC-20	79.32	91.5	86.24	71.8	85.2	88.26
206C						
AW	84.76	90.03	81.22	89.12	83.96	86.97
ALA	59.91	75.85	39.57	80.31	52.06	39.6
PSC	75.71	78.25	68.52	73.08	54.61	76.79
PSS	85.45	86.98	80.6	92.48	77.89	82.69
PSA	68.07	76.43	57.04	93.14	58.42	54.27

Commercial GAC
Bituminous Coal GAC
F200- Filtrasorb 200 (Bituminous coal based)

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Coconut based GAC
GRC-20- Calgon coconut shell based
206C AW-Waterlinks coconut shell based

Chemically activated GAC
PSA- Pecan shell acid-activated
ALA- Almond based acid- as against

Statistical Analysis

Principal component analysis was used to produce a scatter plot of the relationship between the commercial reference GAC (F200, GRC-20, and 206C AW) and experimental GACs (PSA, PSS, PSC, and ALA) in terms of their physical and chemical, as well as adsorption of volatile organic compounds (Figure 4.4). Four quadrants were separated by the intersection of the zero values along the x- and y- axes. The experimental GACs most similar to the reference GACs are expected to cluster in the quadrant containing the latter. Only one experimental carbon PSA clustered around the two reference commercial GACs F200 and 206C AW in the lower left quadrant. ALA and GRC-20 occupied the lower right quadrants, whereas PSC and PSA occupied upper right and upper left quadrants respectively. The dissimilarity of the GRC-20 against the

other two commercial GACs can be mainly attributed to higher adsorptive capacity, higher surface area, and ash content.

Cluster analysis is another multivariate technique that allows grouping of GACs based on similarities using several variables simultaneously.   For cluster analysis both hierarchal (Figure 4.6) and non-hierarchal analysis (Table 4.3) were used.
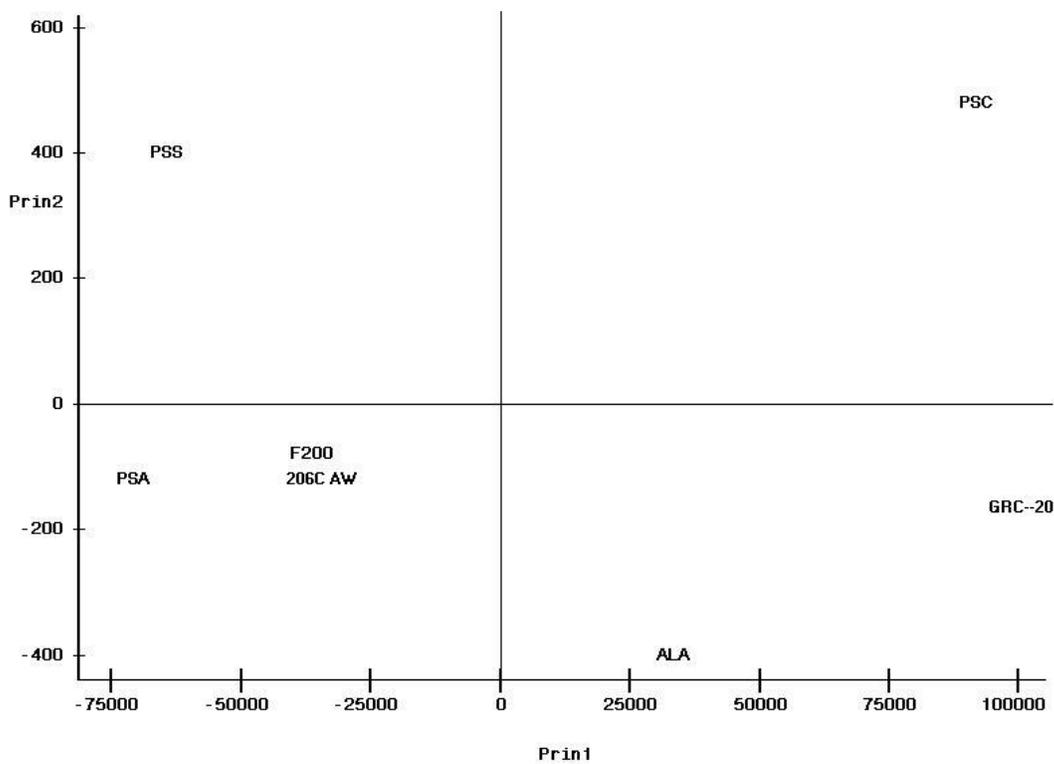

Figure 4.5: Grouping of experimental carbons with commercial carbons by Principal component analysis.

Commercial GAC
Bituminous Coal GAC
F200- Filtrasorb 200 (Bituminous coal based)

Coconut based GAC
GRC-20- Calgon coconut shell based
206C AW-Waterlinks coconut shell based

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated
ALA- Almond based acid-activated

The non-hierarchical clustering presented in Table 4.3 indicates that the grouping of adsorptive and overall properties were very much similar, inferring that adsorptive properties greatly influenced the overall properties. Furthermore, the experimental carbons PSS and PSA, with respect the overall and adsorptive properties, grouped with two commercial carbons F200 and 206C AW in cluster 3.

Groups of physical and chemical properties of carbons varied substantially in that only F200 and PSA clustered similarly in cluster 3. The PSS separately clustering in cluster 1 is attributed to its high conductivity and high pH. Similarly group of PSC in cluster 2 can be attributed to its low surface area and low bulk density.

Table 4.3: Non-hierarchical clustering of GACs based on their physical, chemical, and VOC adsorptive properties.

Basis of clustering	Cluster 1	Cluster 2	Cluster 3
Physical and Chemical Properties of GAC	PSS	PSC	F200 GRC-20 206C AW ALA PSA
Adsorption of VOC	ALA	GRC-20 PSC	F200 206C AW PSS PSA
Overall properties	ALA	GRC-20 PSC	F200 206C AW PSS PSA

Commercial GAC
Bituminous Coal GAC
F200- Filtrasorb 200 (Bituminous coal based)

Coconut based GAC
GRC-20- Calgon coconut shell based
206C AW-Waterlinks coconut shell based

Experimental GAC
Physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated
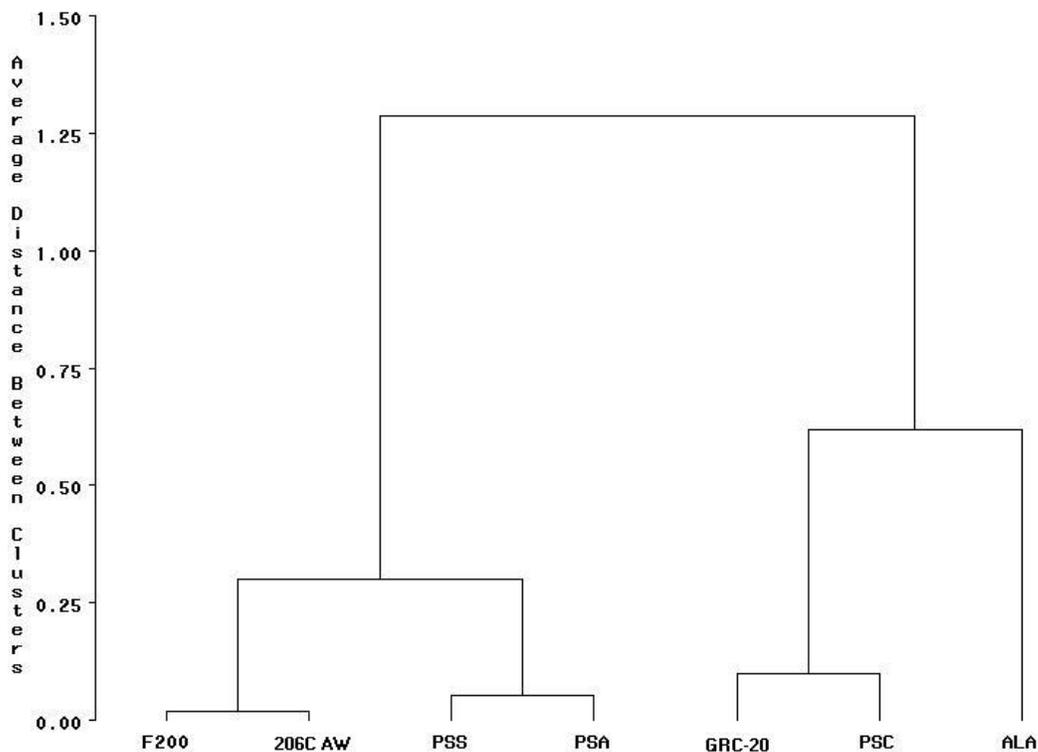**ALA**- Almond based acid-activated

Figure 4.6: Dendogram representation of hierarchy on grouping of activated carbon based on their similarities with respect to overall adsorptive capacity.

Commercial GAC   **Experimental GAC**
Bituminous Coal GAC   *Physically activated GAC*
F200- Filtrasorb 200 (Bituminous coal based)   **PSS**- Pecan Shell Steam-activated
                                                  PSC- Pecan Shell CO_2 activated

Coconut shell-based GAC   *Chemically activated GAC*
ALA- Almond Based Acid-activated   **PSA**- Pecan Shell Acid-activated

GRC-20- Calgon Based Coconut   **ALA**- Almond Based Acid-activated

The hierarchical clustering presented in Figure 4.6 was more selective than either of the two groups (Principal Component Analysis and non-hierarchical clustering). The hierarchical clustering represented in the left wing of the Figure 4.6 was similar in adsorption characteristics of VOCs and overall properties to grouping of F200, 206C AW, PSS and PSA presented in cluster 3, Table 4.5, and grouping of GRC-20 and PSC

presented in cluster 2, Table 4.5. The dissimilarity between hierarchical and non-hierarchical grouping was primarily the formation subgroups in hierarchical cluster of PSS and PSA in one sub-group and F200 and 206C AW in the second sub-group.

4.5 Conclusions

The following conclusions are drawn from this study:

1. The result obtained for COD adsorption indicate that pecan shell-based steam-activated and pecan shell-based acid-activated carbons had higher adsorptive capacities than the pecan shell-based carbon dioxide-activated carbon and Filtrasorb 200 at all the carbon dosages used during the experiment. These carbons were more efficient compared to Filtrasorb-200. Pecan shell-based carbon dioxide-activated carbon proved to have the lowest adsorption efficiency of COD at the chosen concentration levels ranging from 0.01 to 1.5 g/100 ml.

2. The method of activation affected the pH of the experimental carbons.

3. Within the laboratory conditions the present study was conducted, the results indicated that the steam-activated and acid-activated pecan shell-based activated carbons exhibited better adsorption efficiency of COD than the commercial carbons.

4. The physically (steam and carbon dioxide) activated pecan shell-based carbons were superior in their adsorption to chemically activated pecan as well as almond shell-based carbons. Among the commercial carbons it was observed that coconut shell-based activated carbons adsorbed better than the bituminous coal based carbon.

5. All the carbons studied exhibited efficient adsorbability of benzene possibly because of its zero dipole moment.

6. The adsorption of the VOCs by granular activated carbons primarily depends on the carbon precursor, and the method of activation. These two variables affect the surface chemistry of the carbons.

7. The results of the statistical analysis principally concludes that steam-activated pecan and acid-activated pecan shell-based carbon clustered together with the two commercial carbons namely F200, and 206C AW, thus inferring that these experimental carbons could potentially be used as an alternative sources for VOC adsorption in wastewater.

CHAPTER 5
PECAN SHELL-BASED GRANULAR ACTIVATED CARBONS (GACs) FOR TREATMENT OF INORGANIC CONTAMINANTS IN MUNICIPAL WASTEWATER

5.1 Introduction

Contaminants in municipal wastewater are introduced as a result of water usage for domestic, commercial, or institutional purposes; water usage for product processing or cooling purposes within industries discharging liquid effluents into municipal sewerage systems; and infiltration/ inflow and/ or stormwater runoff (Liu and Liptak, 2000). The effects of pollution sources on municipal water quality depend on type and concentration of pollutants. The sources for inorganic contaminants in municipal wastewater include domestic wastes, domestic water supply, ground water infiltration (alkalinity, chlorides, nitrogen phosphorous and sulfur) and commercial and industrial wastes (phosphorous, sulfur, and heavy metals). The effects of these contaminants can be ecological, toxic or harmful health effects to animal, plants and humans. Excessive nitrogen and phosphorous in municipal wastewater lead to algal over growth and can disrupt water treatment processes. Large concentration of chlorides causes salty taste to water and may result in the rusting of treatment equipments. Acids, alkali and heavy metals can be toxic to cause fish kills and create an imbalance in ecosystems.

Activated carbon has long been recognized as one of the most versatile adsorbents to be used for the effective removal of organic contaminants in wastewater treatments. Charcoal, the forerunner of modern activated carbon whose ability to purify water dates back to 2000 B.C. Lately during the past few decades, there has been an increased awareness of the existence of organic and inorganic pollutants and their toxic effects in natural water. Consequently, urgent need has been exhibited by various public and health

agencies for the removal of these contaminants in stream and natural water and has resulted in the emergence of activated carbon adsorption as one of the most effective methods for removing these contaminants in wastewater treatments.

Activated carbons are produced from various carbonaceous materials such as wood, coal, peat, lignite, saw dust, sugarcane bagasse, and petroleum coke. However, materials such as rice hull, peat, sawdust and wood consists of soft compressible waste product of low density and need binders. Nutshells from pecan, almond, walnut, and macadamia are hard, dense, not easily compressed and do not need binder and are more suitable for producing granulated carbons.

The production of activated carbon involves two processes; carbonization also called pyrolysis which consists of heating and converting the raw material to char in the absence of air, to temperatures usually below 600°C. During carbonization volatile substances are removed from the raw materials leaving the residue as char or coke. Activation consists of treating the pyrolized raw material (char) with oxidizing agent with steam, carbon dioxide (physical activation) or by an acid such as nitric acid (chemical activation). During activation, the oxidizing agents selectively attack portions of the char, allowing the gaseous volatiles to escape and resulting in the formation of hollow pores in the char. The activation process has a decisive effect on a most important property, i.e., adsorption, of the activated carbon.

Although, various carbonaceous materials are used in the production of activated carbons, abundance availability and low cost of agricultural by-products make them good candidates and sources of raw materials for activated carbons. The annual harvesting and processing of various agriculture crops grown in the United States yield considerable

quantities of agriculture by-products. The United States produced 93 billion lbs of

sugarcane, 213 million lbs of rough rice, 315 million lbs of pecan, and 850 million lbs

almonds in year 2001 (Agricultural Statistics, 2002). Some of the commodities, which

produce these by-products, are from major agricultural crops; sugarcane, rice, and pecans

come from Louisiana farms. These agricultural by-products have little or no economic

value, and their disposal not only is costly but may also cause environmental problems.

Published literature (Mitchelle et al., 1998; Johns et al., 1998; Ahmedna et al., 2000(a)) to

show that these by-products are potential raw material for preparing carbonaceous

adsorbents. Conversion of these agricultural by-products into activated carbons which

can be used as adsorbents such as in wastewater treatment, in the treatment of industrial

and municipal effluents would add value to these agricultural commodities, help reduce

the cost of waste disposal, and provide a potentially cheap alternative to existing

commercial carbonaceous adsorbents. A comprehensive review of literature has shown

that nutshell-based (such as pecan, almond, and macadamia) activated carbons are as

good in their adsorption ability, in some instances better than commercial carbons, and

can be produced almost at half the cost (Ng, 2001).

Therefore the present investigation was undertaken to evaluate the adsorption

effectiveness of pecan and almond shell-based granular activated carbons (GACs) in

removing inorganic contaminants in municipal wastewater. The adsorption behaviors of

these GACs were compared to adsorption performance of commercial carbon namely,

Filtrasorb 200. The investigation focused on the isotherms of metal ions in a multi

component test medium (to understand preferential and selective adsorption of the carbon

sites will have towards specific metals) and the effect of pH on the adsorptive capacity of

the carbons (to facilitate the selection under buffered conditions). The test medium consisting of various inorganic compounds was formulated to resemble as closely as possible to a real world municipal wastewater. Use of test medium was helpful in eliminating the affect of unknown interfering substances generally present in municipal water and also in the interpretation of experimental results.

5.2 Materials

Four activated carbons consisting of three experimental carbons, namely (i) Pecan shell- steam activated (ii) Pecan shell- carbon dioxide activated, and (iii) Pecan shell- acid activated were produced at USDA, Southern Regional Research Center, New Orleans, LA, and were furnished for analysis. One commercial carbons, namely Filtrasorb-200 (Calgon Corporation) was selected for this experiment. Cupric Sulfate ($Cu_2SO_4.5H_2O$) was from Fisher Pittsburgh, PA, Zinc Chloride ($ZnCl_2$), and Lead Nitrate ($Pb(NO_3)_2$), Nitric acid were from Sigma Aldrich, WI. The pH of the solution was measured by Orion model 410-pH meter (Orion Research Inc., Boston, MA).

5.3 Methods

5.3.1 Preparation of Inorganic Stock Solution

A working standard stock solution consisting of 0.5 mM of each of the $Cu_2SO_4.5H_2O$, $ZnCl_2$, and $Pb(NO_3)_2$ in an acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid) was prepared. The initial pH of the solution was 4.8.

5.3.2 Pretreatment of GACs Prior to Adsorption Study

In order to reduce the conductivity, which interferes in the adsorption of the inorganic salts, the GACs were pre-washed with distilled deionized water and oven dried at $110 \pm 5°C$ overnight.

5.3.3 Adsorption Study

The adsorption study consisted of mixing activated carbons to a 100 ml working standard solution in a 125 ml polyvinyl chloride container. The carbon dosages used in this study were 0.05, 0.1, 0.3, 0.5, 0.75, and 1.0 g per 100 ml of the working solution. The mixture of activated carbon and the solution was stirred at 500 rpm using a Teflon coated ½ in. bar on a Corning magnetic stirrer. In each of the experiments the carbon solution mixture was stirred for 24 h. At the end of the specified period, the samples were removed from the corning magnetic stirrer and pH of the solution was measured by using Orion model 410 pH meter. Thereafter, an aliquot of the solution was obtained by a disposable syringe and filtered using PTFE 0.45μm filter. The filtrate was stored in refrigerator and subsequently analyzed for the residual inorganic salts by using Inductively Coupled Plasma, ICP (Optima 3000, Perkins Elmer).

5.4 Results and Discussion

5.4.1 Residual Inorganic Salts in Treated Solution

In Figures 5.1, 5.2, 5.3 respectively, are presented, the percentage removal of Cu^{2+}, Pb^{2+}, and Zn^{2+} ions by experimental and commercial carbons.

The data from Figure 5.1 indicates that for all the carbon dosages used in this study, the adsorption of Cu^{2+} ion by steam-activated pecan shell-based GAC reached relatively the highest level compared to the adsorption levels of other experimental and commercial carbons. Filtrasorb 200 competitively adsorbed Cu^{2+}, comparable to that of acid-activated pecan shell-based carbon dioxide-activated carbon, but poorly adsorbed Pb^{2+}, and Zn^{2+} with respect to the experimental carbons. Acid-activated pecan shell-based carbon showed higher adsorption capacity as against the physically activated pecan

shell-based carbons (PSS and PSC) and commercial carbon (F200) with respect to Pb^{2+} and Zn^{2+} adsorption under the carbon dosages used for the study. All the three experimental carbons performed better than the commercial carbons. It was also observed that the adsorption rate was $Pb^{2+} > Cu^{2+} > Zn^{2+}$. This could possibly be related to their electronegativity, inferring that highly electronegative ions have greater tendency for adsorption on the active sites of the carbon.

In Figure 5.4 is presented the data on the effect of buffering (0.07 M sodium acetate and 0.03 M Acetic acid) on the pH of the inorganic stock solution during the various carbon dosages (g of carbon/100ml inorganic stock solution). The data showed that throughout the carbon dosage studied, the pH of the stock solution did not change when it was treated with PSA, PSC, and F200. However, for the PSS carbon dosages between 0.0 to 0.8 g/ml, the pH of the inorganic stock solution increased from 5.5 to 6.6, and considerably larger increase (6.6 to 8.0) during changes in the carbon dosage from 0.8 to 1.0 g/ml.

5.4.2 Freundlich Isotherms

The data on the effects of carbon dosage and three experimental and one commercial carbon on the three metal ions adsorption of the test medium were fitted to a Freundlich model. Graphical representation of this model showing the adsorption isotherms of pecan shell activated carbons and control carbons on metal ions is presented in Figure 5.5, 5.6, and 5.7. The values for constants k and 1/n of the Freundlich equation are presented in Table 5.1.

The Cu^{2+} ion adsorption presented in Figure 5.5 shows that steam-activated pecan shell-based carbon with higher log x/m (solute adsorbed/ carbon dosage) ratio and log Ce
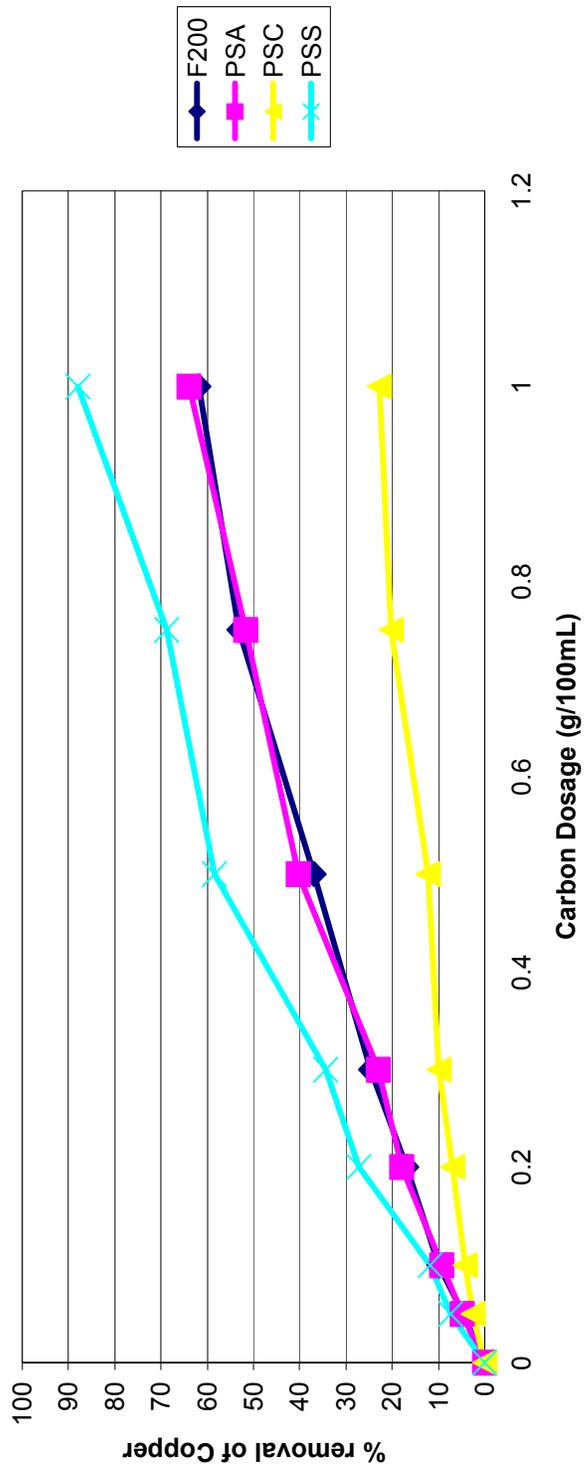
Figure 5.1: Percentage removal of Cu^{2+} ion by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
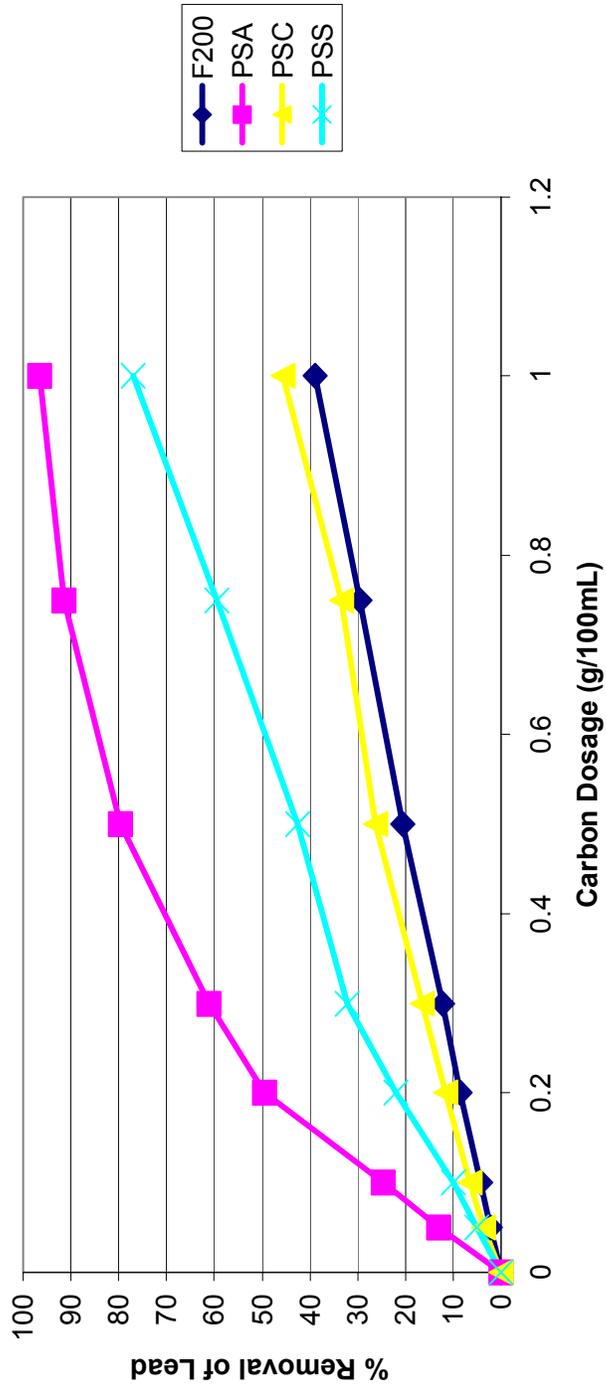PSA- Pecan shell acid-activated

Figure 5.2: Percentage removal of Pb^{2+} ion by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

72

Figure 5.3: Percentage removal of Zn^{2+} ion by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
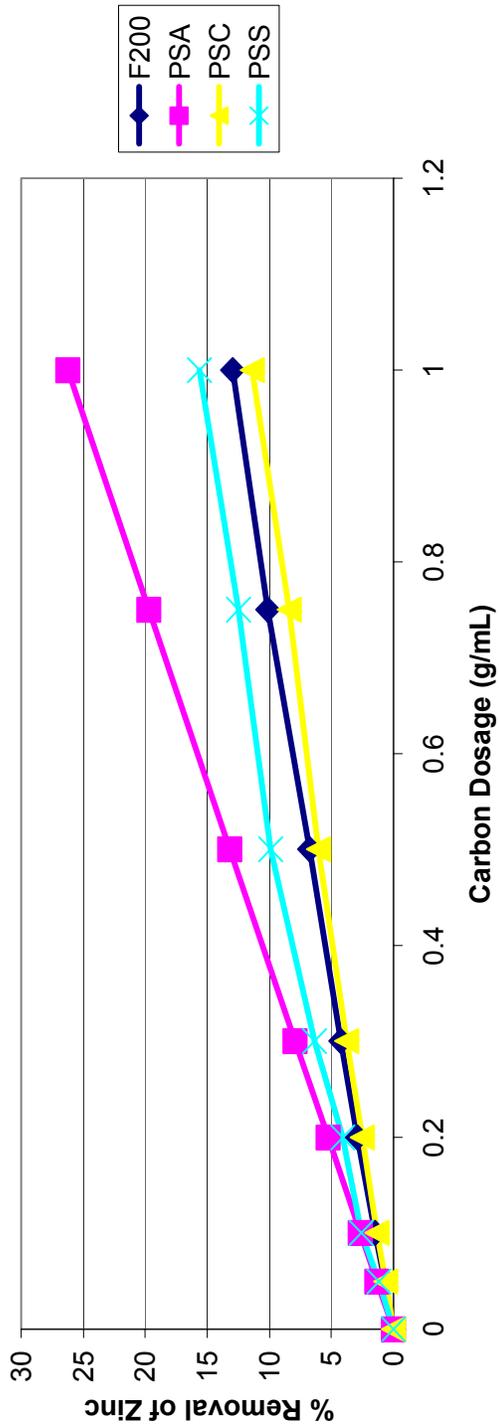PSA- Pecan shell acid-activated

73

Figure 5.4: Final pH of the solution at different carbon dosage after the treatment time.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
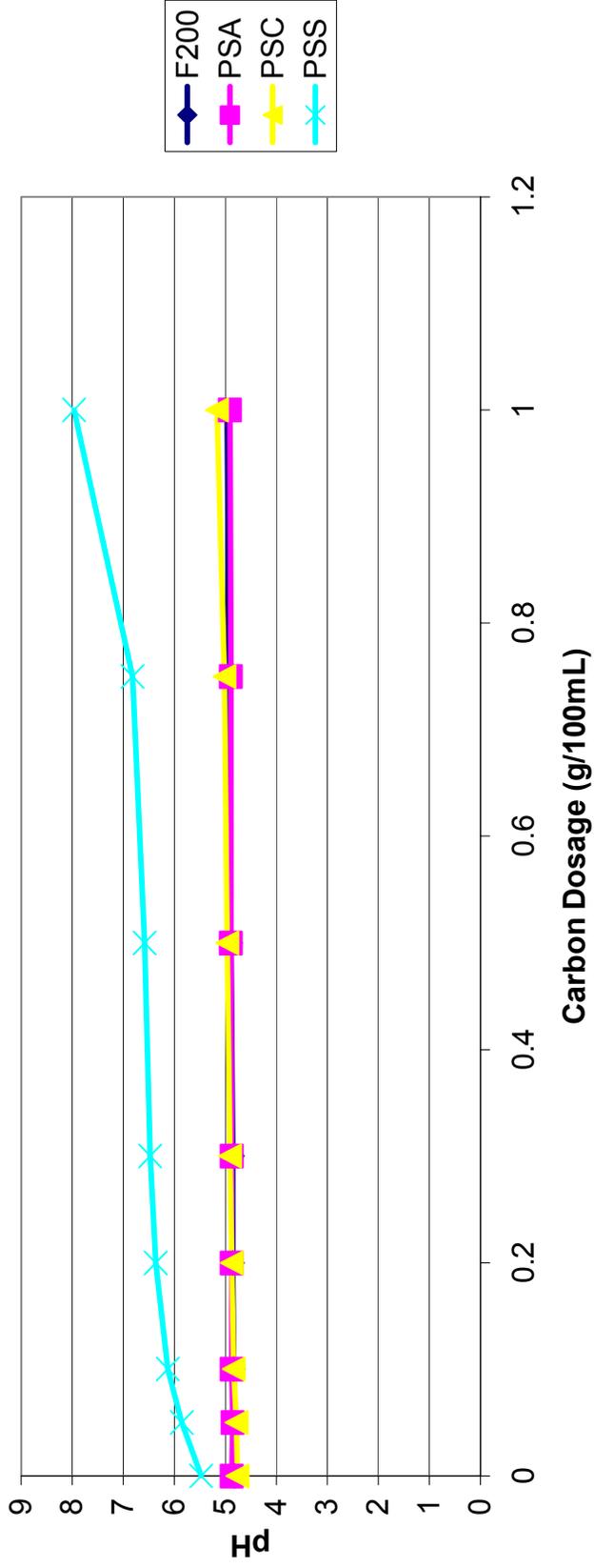PSA- Pecan shell acid-activated

ranging from 0.5 to 1.0 g/100 ml is most suitable for the adsorption of Cu^{2+}. The adsorption curve for acid-activated pecan shell-based carbons and Filtrasorb 200 were similar and therefore had same adsorptive potential within the dosage levels under study. The slope for carbon dioxide-activated pecan shell-based carbon was sharp (2.7652) which represents greater efficiency at higher residual concentrations and hence efficiency at lowers residual concentrations. In case of Pb^{2+} adsorption, Filtrasorb 200 and carbon dioxide-activated pecan shell based carbons had much lower k value (14.5512 and 1.9426, respectively) than acid- and steam-activated pecan shell-based carbons (64.18 and 34.696). This means that the adsorptive efficiency of these two carbons were good only at a very low ion concentrations. Zn^{2+} adsorption by carbon dioxide-activated pecan shell-based activated carbon was at lower level of x/m ratio and had steeper slopes (1.3032), which infer that the PSC, can surpass the Filtrasorb 200 carbon. However, the acid and steam-activated pecan shell-based carbons were at higher level of x/m ratio and had lower slopes (0.0392 and 2.7954, respectively), emphasizing that these carbon were effective only for the adsorption for the given range of carbon dosage level used in this investigation.

5.5 Conclusions

The results obtained from this study indicate:

1. In regards to adsorption of Cu^{2+} ion, the experimental carbons PSA performed as effectively as the commercial carbon F200.

2. In regards to the adsorption of lead and zinc, all the three experimental carbons (PSA, PSS, and PSC) performed better than commercial carbon. However, within the four
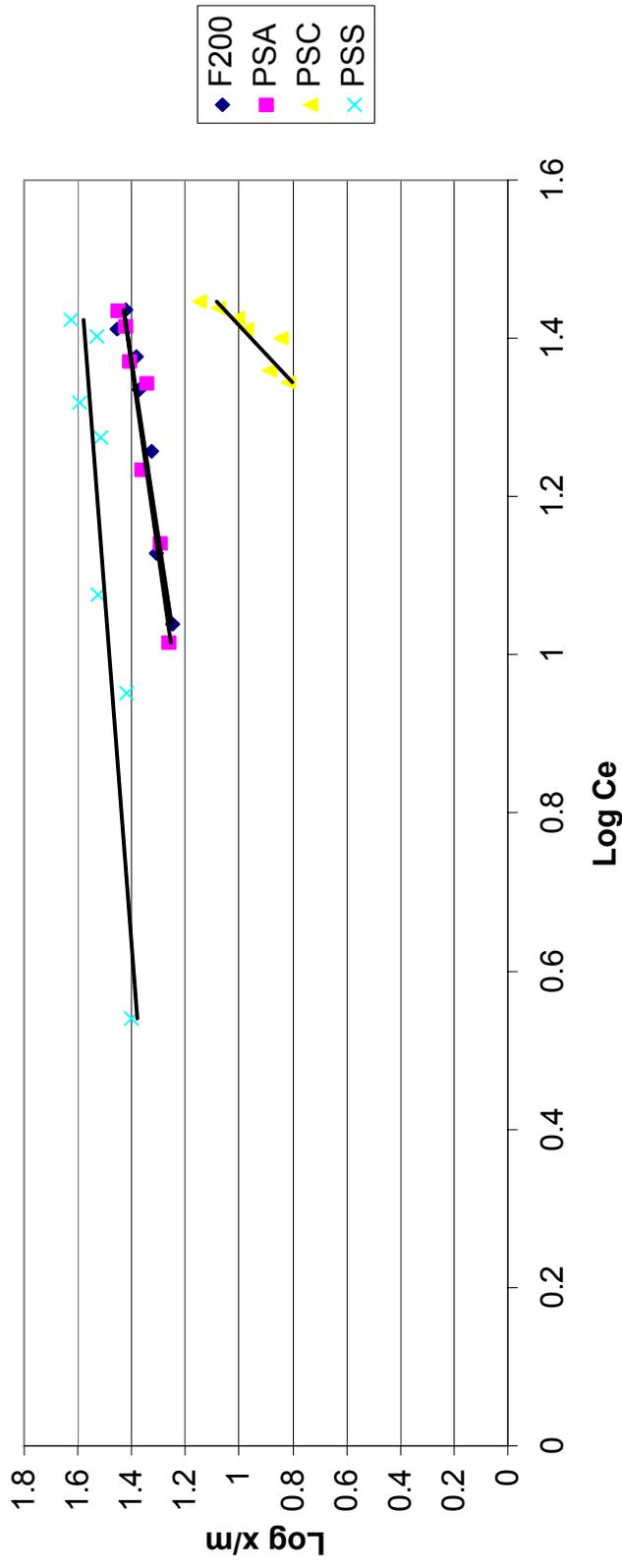
Figure 5.5: Freundlich Isotherms for the Cu^{2+} adsorption by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

Figure 5.6: Freundlich Isotherms for the Pb^{2+} adsorption by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan shell CO_2 activated

Chemically activated GAC
PSA- Pecan shell acid-activated

Figure 5.7: Freundlich Isotherms for the Zn^{2+} adsorption by granular activated carbons.

Commercial GAC
Bituminous coal based
F200- Filtrasorb 200

Experimental GAC
physically activated GAC
PSS- Pecan shell steam-activated
PSC- Pecan Shell CO_2 activated

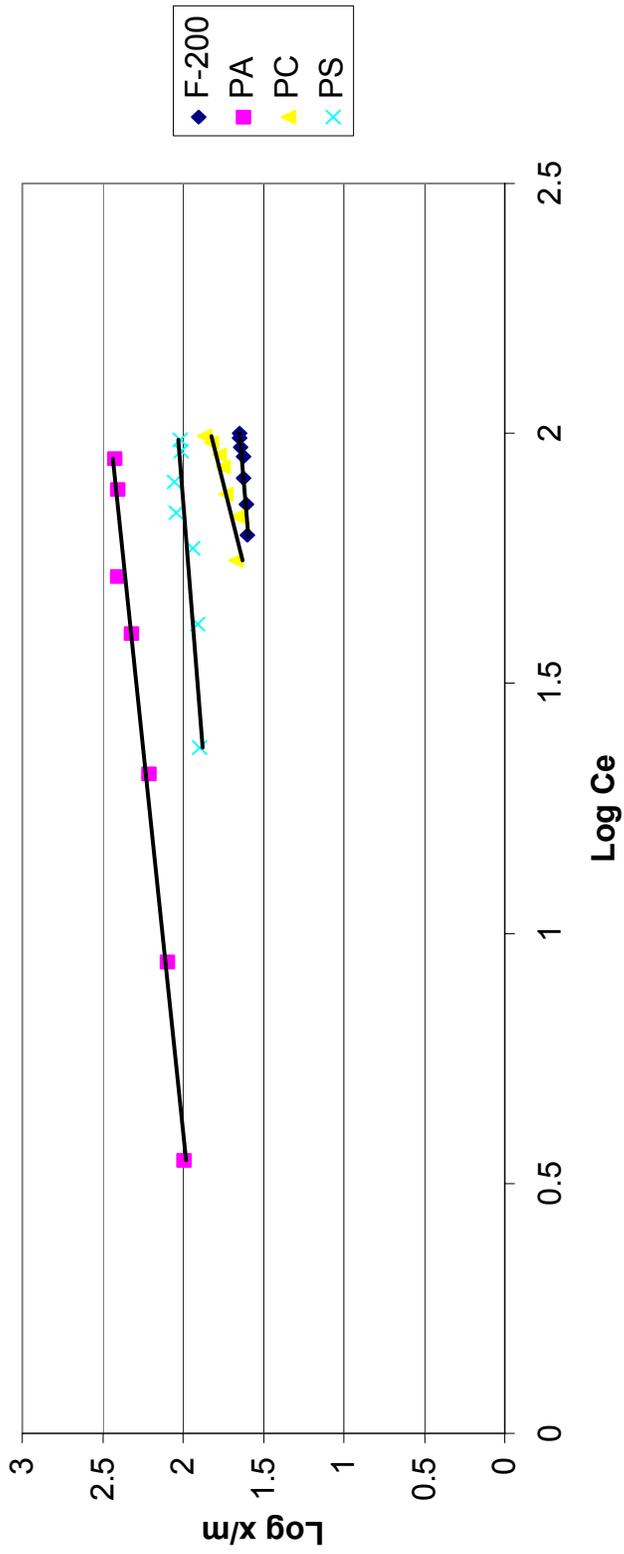*Chemically activated GAC*
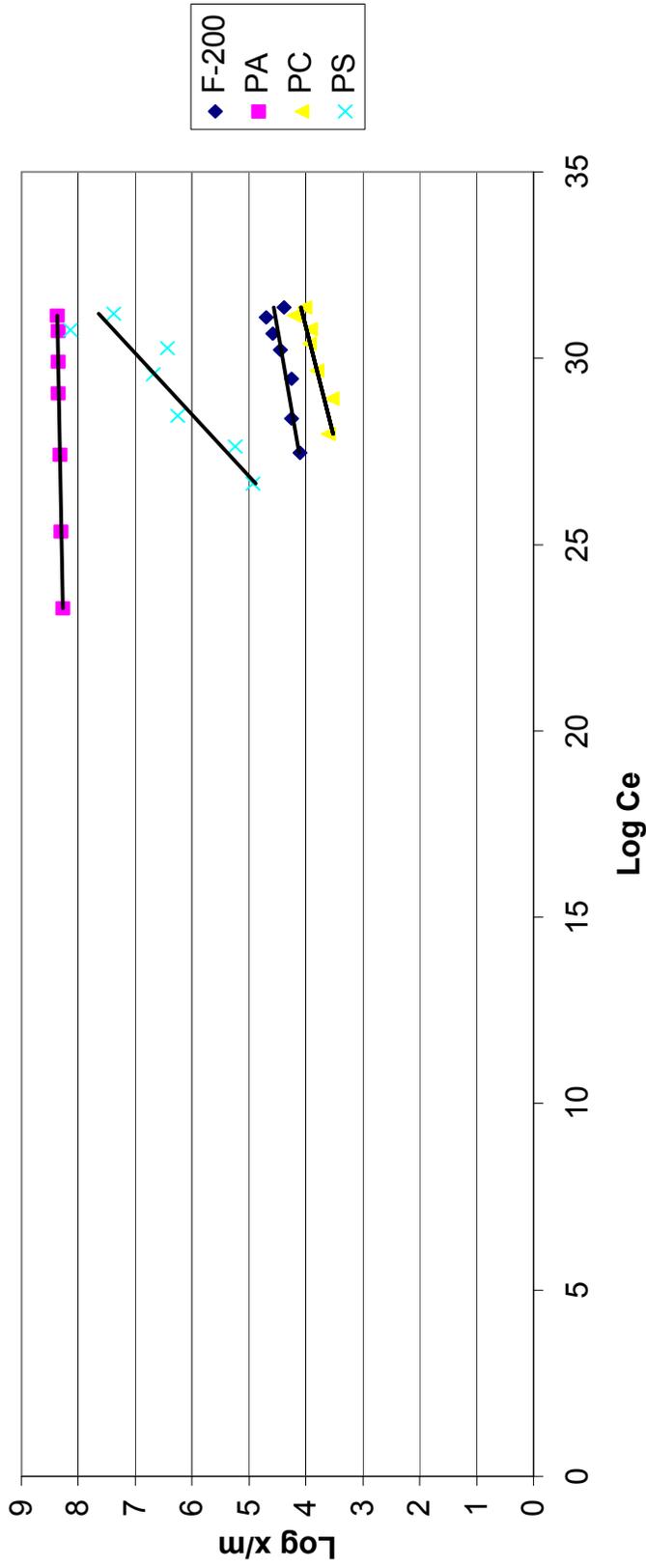PSA- Pecan shell acid-activated

Table 5.1 Freundlich constants derived from the adsorption isotherm plots of respective metal ions.

Metal ion	Carbon type	1/n	k	r
Cu^{2+}	F200	0.4471	6.0995	0.9162
	PSA	0.4126	6.8454	0.8822
	PSC	2.7652	0.0012	0.7818
	PSS	0.2256	18.1217	0.7483
Pb^{2+}	F200	0.2414	14.5512	0.8944
	PSA	0.322	64.1800	0.9831
	PSC	0.77	1.9426	0.8215
	PSS	0.2474	34.696	0.7203
Zn^{2+}	F200	0.8036	0.2868	0.9767
	PSA	0.0392	0.0392	0.9309
	PSC	1.3032	6.6206	0.8209
	PSS	2.7954	7.3756	0.8678

Experimental GAC
Physically activated GAC
PSS- Pecan shell-based steam-activated
PSC- Pecan shell-based CO_2 activated
Chemically activated GAC
PSA- Pecan shell-based acid-activated

Commercial GAC
F200- Filtrasorb 200 (Bituminous coal-based)
n and k are dimensionless constants of Freundlich model; r: linear correlation coefficient.

carbons used for the adsorption of Pb^{2+} and Zn^{2+}, PSA was found to be more effective against PSS and PSC.

3. The pH of the steam-activated pecan shell-based carbon increased considerable (6.6 to 8.0) between carbon dosages with differences of 0.8 to 1.0 g/100ml.

4. The steam-activated pecan shell-based carbon with higher log x/m (solute adsorbed/ carbon dosage) ratio and log Ce ranging from 0.5 to 1.5 is most suitable for the adsorption of Cu^{2+} (Figure 5.5).

5. Filtrasorb 200 and carbon dioxide-activated pecan shell-based carbons had much lower slope (0.2414 and 0.77, respectively) than acid- and steam-activated pecan shell-based carbons (0.322 and 0.2474) with respect to Pb^{2+} adsorption (Figure 5.6).

6. Filtrasorb 200 was at lower level of x/m ratio and had steeper slope (0.8036) for Zn^{2+} adsorption (Figure 5.7).

CHAPTER 6
SUMMARY AND CONCLUSIONS

The results of this investigation are summarized as follows:

1. The results suggest that, among the three commercial carbons used, the coconut shell-based GRC-20 carbon, manufactured by Calgon Corporation, had the largest total surface area with 1038 m^2/g, followed by another coconut shell-based carbon 206C AW at 898 m^2/g, manufactured by Waterlinks Corporation. The lowest total surface area of 835 m^2/g, found among the commercial samples used in this investigation was of Filtrasorb-200 (F200), which is a coal-based carbon. Almond shell-based chemically activated granulated carbon (ALA) had the largest total surface with 1340 m^2/g, followed by steam-activated pecan shell-based carbon with 917 m^2/g and acid-activated pecan shell-based carbon with 902 m^2/g and carbon dioxide-activated pecan shell-based carbon with 435 m^2/g.

2. In regard to the bulk density of the experimental carbons, the data indicate that the carbon PSC (pecan shell-based physically activated by carbon dioxide) had the highest value (0.57 g/m^3) followed by PSA (0.51 g/m^3), PSS (0.49 g/m^3), and ALA (0.3 g/m^3).

3. Acid-activated pecan shell carbon, PSA showed the lowest attrition (7.1 %) among experimental carbons, followed by physically activated pecan shell-based carbons such as carbon dioxide-activated pecan shell-based carbon, PSC (12.79 %), steam-activated pecan shell-based carbon, PSS (22.15 %) and acid-activated almond shell based carbon ALA (31.68 %).

4. The ash content study indicated that, carbon dioxide activated pecan shell-based carbon had the highest ash content (6.00%) followed by steam-activated pecan shell-

based carbon (5.53%), acid-activated almond shell-based carbon (3.35%), and acid-activated pecan shell-based activated carbon (1.42%).

5. Acid-activated carbons such as almond shell-based carbons (ALA) and pecan shell-based carbon (PSA) had acidic pH, 6.08 and 5.70, respectively and physically activated experimental carbons such as carbon dioxide-activated pecan shell-based carbon and steam-activated pecan shell-based carbon (PSS) had basic pH, 10.07 and 10.01, respectively.

6. Physically activated experimental carbons (PSC and PSS) had high conductivity values consisting of 330.66 µS and 752.76 µS, respectively. Chemical activated experimental carbons (ALA and PSA) showed lower conductivity than the physically activated carbons, with conductivity values of 27.11 µS and 46.03 µS, respectively.

7. Principal component analysis results indicated that acid-activated pecan shell-based carbons (PSA) grouped with the commercial carbons (F200, GRC-20, and 206C AW) in all the parameters analyzed thus emphasizing its closeness to the commercial carbons.

8. The COD adsorption study showed that, pecan shell-based acid-activated and steam-activated showed better adsorbability whereas carbon dioxide-activated carbon proved to be the lowest adsorption efficiency of COD at the chosen concentration levels ranging from 0.01to 1.5 g/100 ml.

9. The VOC adsorption study indicated that, all the carbons studied exhibited efficient adsorbability of benzene possibly because of its zero dipole moment.

10. The results of the statistical analysis principally concludes that steam-activated pecan and acid-activated pecan clustered together with the two commercial carbons namely

F200, 206C AW, thus inferring that these experimental carbons could potentially be used as an alternative sources for VOC adsorption in wastewater.

11. The inorganic adsorption of stock solution indicated that, for all the carbon dosages used in this study the adsorption of Cu^{2+} ion by steam-activated pecan shell-based GAC reached relatively the highest level compared to the adsorption levels of other experimental and commercial carbons. Acid-activated and steam-activated pecan shell-based carbons performed efficiently with respect to Pb^{2+}, and Zn^{2+} ion adsorption.

Based upon the above results, the following conclusions were drawn:

1. Almond shell-based chemically activated carbon had significantly (5% significance) larger total surface area than F200 (Filtrasorb 200), GRC-20 (Calgon coconut based carbon), and 206C AW (Waterlinks coconut based carbon).

2. The overall bulk density result indicate that pecan shell-based granular activated carbon were comparable to the commercial carbons.

3. ALA showed the highest attrition value thereby making it undesirable because of its susceptibility to abrasion losses during commercial utilization.

4. Acid-activated pecan shell-based carbon (PSA) had the lowest ash content making it most desirable carbons of all the carbons analyzed for this study followed by Waterlinks coconut shell-based carbon.

5. The pH of the experimental carbons mainly depended on the activation process.

6. Conductivity of all the experimental carbons was significantly (5% significance) higher than the commercial activated carbons.

7. The method of activation affected the pH of the experimental carbons.

8. Steam-activated and acid-activated pecan shell-based carbons are preferable to commercial carbons in adsorbing COD level under laboratory conditions.

9. With respect to the VOC adsorption, physically activated pecan shell based carbons (steam and carbon dioxide) were superior in their adsorption to chemically activated pecan as well as almond shell based carbons.

10. The adsorption of the VOCs by granular activated carbons primarily depends on the carbon precursor, and the method of activation. These two variables affect the surface chemistry of the carbons.

11. Filtrasorb 200 competitively adsorbed Cu^{2+}, comparable to that of acid-activated carbon dioxide-activated carbon pecan shell-based carbons, but poorly adsorbed Pb^{2+}, and Zn^{2+} with respect to the experimental carbons. Acid activated pecan shell-based carbon showed higher adsorption capacity against the physically activated pecan shell-based carbons (PSS and PSC) and commercial carbon (F200) with respect to Pb^{2+} and Zn^{2+} adsorption under the carbon dosages used in this study. All the three experimental carbons performed better than the commercial carbons. It was also observed that the adsorption rate was $Pb^{2+} > Cu^{2+} > Zn^{2+}$. This could possibly be related to their electronegativity, inferring that highly electronegative ions have greater tendency for adsorption on the active sites of the carbon.

12. Based on the overall results of the study concerning organic (COD, and VOCs) and inorganic (metal ions), it is suggested that experimental carbons could be a viable and cost effective option against commercial carbons in municipal wastewater treatment systems.

REFERENCES

Agricultural statistics 2002. 2002. USDA, National Agricultural Statistics Service, U.S. Government Printing Office. Washington D.C.

Ahmedna, M., 1998. Granular activated carbon from agriculture by-products: Carbon properties and their relation to sugar decolorization potential. PhD. dissertation, Louisiana State University, Baton Rouge, Louisiana.

Ahmedna, M., Johns, M., M., Clarke, S.J., Marshall, W.E., and Rao, R.M., 1997. Potential of agricultural by-product based activated carbons for use in raw sugar decolorization. Journal of the Science of Food and Agriculture. 75, 117-124.

Ahmedna, M., Marshall, W.E., and Rao, R.M. 2000 (a). Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical, and adsorptive properties. Bioresource Technology. 71(2), 113-123.

Ahmedna, M., Marshall, W.E., and Rao, R.M. 2000 (b). Surface properties of granular activated carbons from agricultural by-products and their effect on raw sugar decolorization. Bioresource Technology. 71(2), 103-112.

AWWA Standards for granular activated carbon. 1991. American water works association, Denver, CO.

Clesceri, L.S., Greenberg, A.E., and Eaton, A.D., 1998. Standard Methods for the examination of water and wastewater. American public health association. Washington D.C. pp. 5-17- 5-18.

Braunauer, S., Emmette, P., and Teller, E., 1938. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society. 60, 309-319.

Butterworth S. L. and Sember J. D. 1993. Wastewater: Emphasis Shifting to Toxicity Reduction; Granular activated carbon is one treatment technology used to reduce toxicity in wastewater. 25 (11), 70-72.

Dastgheib, S.A., and Rockstraw, D.A. 2001. Pecan shell activated carbon: Synthesis, characterization, and application for the removal of carbon from aqueous solution. Carbon. 39(12), 1849-1855.

Eckenfeldr Jr. W.W. ed. 1981. Application of Adsorption to wastewater treatment. Enviro Press Inc. TN.

Faust S. and Aly O.M. ed. 1998. Chemistry of water treatment. 2nd ed. Ann Arbor Press Michigan.

Girgis, B.S., Khalil, L.B., and Tawfik, T.A.M., 1994. Activated carbon from sugarcane bagasse by carbonization in the presence of inorganic acids. Journal of Tech. Biotech. 61 (1), 87-92.

Hassler J. W. 1963. Activated Carbon. 2nd ed. Chemical Publishing Company, Inc. NY.

Johns, M.M., Marshall, W.E., and Toles, C.A. 1998. Agriculture by-products as granular activated carbons for adsorbing dissolved metals and organics. 1998. 71(2), 131-140.

Johns, M.M., Marshall, W.E., and Toles, C.A. 1999.The effect of activation method on the properties of pecan shell-activated carbons. Journal of Chemical Technology and Biotechnology. 74(11), 1037-1044.

Liu, D.H.F., and Liptak, B.G. 2000. Wastewater Treatment. Lewis Publishers. Boca Raton, FL.

Mitchelle, J.M., Marshall, W. E. and Toles, C.A. 1998. Agricultural By-products as Granular Activated carbons for Adsorbing Dissolved Metals and Organics. Journal of Chemical Technology and Biotechnology. 71(2), 131-140.

Najm, I., Snoeyik, V., Suidan, M. Lee, C., Richard, Y. 1990. Effect of particle size and background natural organics on the adsorption efficiency of PAC. Journal of American water works association. 82 (1), 65-72.

Ng, C. 2001. Use of agricultural by-product based granular activated carbon for the adsorption of geosmin and process and economic analysis for their production. M.S. Thesis. Louisiana State University. Baton Rouge. Louisiana.

Pendyal, B., Johns, M.M., Marshall, W.E., Ahmedna, M. and Rao, R.M. 1999. Removal of sugar colorants by granular activated carbons made from binders and agricultural by-products. Bioresearch Technology. 69, 45-51.

Perrich, J.R., 1981. Activated carbon adsorption for wastewater treatment. CRC press Inc. Boca Raton Fl.

Randtke, S.J., and Snoeyink V.L. 1983. Evaluating GAC adsorptive capacity. Journal of American Water Works Association. 75 (8), 406-413.

Smisek, M., and Cerny, S., 1970. Active Carbon: Manufacture, Properties, and Application. American Elsevier Publishing Co., Inc., New York.

Stenzel, M.H., 1993. Removal of Organics by activated carbon adsorption. Chemical Engineering Progress. 89 (4), 36-43.

Stenzel, M.H., and Gupta S. U., 1995. Hazardous Waste Management. Journal of Air Pollution Control with Granular activated Carbon and Air Stripping. 35 (12), 1304-1309.

Toles, C.A., Marshall W.E., and Johns M.M., 1997. Granular activated carbons from nutshells for the uptake of metals and organic compounds. Carbon 35 (9), 1407-1414.

Toles, C.A., Marshall, W.E., and Johns, M.M., 1998. Phosphoric acid activation of nutshells for metals and organic remediation: Process optimization. Journal of Chemical Technology and Biotechnology. 72(30, 255-263.

Toles, C.A., Marshall, W.E., and Johns, M.M., 1999. Surface functional groups on acid-activated nutshell carbons. Carbon. 37(8), 1207-1214.

Toles, C.A., Marshall, W.E., Johns, M.M., Wartelle, L. H. and McAloon A., 2000. Acid-activated carbons from almond shells: Physical, chemical and adsorptive properties and estimated cost of production. Bioresource Technology. 71(1), 87-92.

U.S. Environmental Protection Agency. 1973. Process design manual for carbon adsorption. U.S.E.P.A. National environmental Research center, Cincinnati, OH.

Wartelle, L.H. Marshall, W.E., Toles C.A., and Johns, M.M. 2000. Comparison of nutshell granular activated carbons to commercial adsorbents for the purge-and trap gas chromatographic analysis of volatile organic compounds. Journal of Chromatography A. 879, 169-175.

Wartelle, L.H., and Marshall, W.E. 2001. Nutshells as Granular Activated Carbons: Physical, Chemical and Adsorptive Properties. Journal of Chemical Technology and Biotechnology. 76, 451-455.

Weber, W.J., 1981. Concepts and principles of carbon application in wastewater treatment. In Eckenfelder, W.W., Application of adsorption to wastewater treatment. CBI Publishing Co. Inc. pp. 5-28.

VITA

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