Characterization of a Novel Biodegradable Material to reduce emission of ammonia

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Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University in partial

fulfillment of the requirements for the degree of

Master of Science

in

Biological Systems Engineering

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December 6, 2007

Blacksburg, Virginia

Keywords: Corn cob, Adsorption, Chemisorption, Physisorption, Steam Explosion

ABSTRACT

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A novel biodegradable ammonia control material was developed from steam exploded corn cob and its adsorption capacity was studied by packed column and titration method. The packed column studies showed that the maximum absorption capacities of the raw corn cob (RCC) and the steam exploded corn cob (SECC) were 10.45 mg NH_3/gRCC and 59.80 mg NH_3/gSECC respectively. However, the titration of the water slurries with a NH_4OH showed that the capacity of the SECC was 14.4 times that of RCC. The large difference between the packed column (SECC/RCC = 5.7) and the slurry titration (SECC/RCC = 14.4) was probably because: (1) the initial ammonia reaction products blocked the pores of the SECC and reduced diffusion into the pore structure; (2) the ammonia gas flow rates were too high and therefore the gas did not penetrate the pores; (3) the gas contact time was below the equilibrium value; and (4) since interior pore surface area is usually larger than the external surface area of a particle, it appears the low column SECC/RCC ratio is due to reactions on the SECC particle surface whereas the slurry result was a combination of both.

Fourier Transform Infrared, FTIR spectroscopy was conducted on RCC, SECC, ammonia adsorbed on RCC and ammonia adsorbed on SECC in the range 4000–700 cm^{-1}. The FTIR bands in the region between 1500 and 2000 cm^{-1} showed a considerable difference between RCC and SECC. When SECC was treated with ammonia, the carboxylic

functional group peak at 1700 cm^{-1} was reduced and a new peak was observed at 1584 cm^{-1}. The adsorption, desorption test and the heat of adsorption results suggested combined physisorption and chemisorption of ammonia on SECC but chemisorption was found to play an important role in ammonia removal. The BET specific surface area of RCC was 3.4 m^2/g whilst that SECC was less than 1 m^2/g. Although SECC had a low surface area compared with RCC its adsorption capacity was found to be greater than that of RCC meaning the adsorption process is chemically controlled. Also, the pore size distribution showed that RCC exhibited both macroporosity and mesoporosity whilst SECC showed only mesoporosity. It is interesting to note that upon steam exploding RCC, the macropores within RCC collapsed to form more mesopores in SECC. The high uptake of SECC was determined to be its small pore width compared to that RCC.

Simultaneous Differential Scanning Calorimetri, DSC and Thermal Gravimetric Analyzer, TGA, was used to determine the heat of adsorption of ammonia on SECC. The heat of adsorption of ammonia on SECC was 33.00 kJ per mole of NH$_3$. This study shows that SECC could be potentially used to remove NH$_3$ from various emission sources.

Keywords: Corn cob, Adsorption, Chemisorption, Physisorption, Steam Explosion

DEDICATION

I dedicate this research work to my mother, Lina and my father, Samuel for believing in me, for their amazing love and being there for me always. I also want to dedicate this to my fiancé, Portia, who has been supportive of me in every step of the way and to my siblings for their wonderful encouragement. To you Dr. Senanu Ashiboir, you are a gem and I will always treasure your pieces of advice.

ACKNOWLEDGMENTS

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NOMENCLATURE

ACC   Activated Coconut Carbon

AFOs   Animal Feeding Operations

ASTM   American Society for Testing and Materials

ATR   Attenuated Total Reflection

BET   Brauner–Emmet–Teller

DFT   Differential Functional Theory

DSC   Differential Scanning Calorimetric

FTIR   Fourier-Transform Infrared

RCC   Raw Corn Cob

SECC   Steam Exploded Corn Cob

TGA   Thermal Gravimetric Analyzer

IUPAC   International Union of Pure and Applied Chemistry

CHAPTER ONE

INTRODUCTION

1.0 Background

In recent years, there has been an increasing emphasis on controlling ammonia emissions because of its deleterious effect on the soil, water, animal and human health. The worldwide emissions of ammonia have been estimated annually at 25 to 35 million tonnes (Karel et al., 2006). The major sources of ammonia include livestock farming including pig and poultry farms. Other sources of ammonia emission include direct volatilisation from mineral fertilizers (particularly urea), agricultural crops and a wide range of non-agricultural sources including sewage, catalytic converters, wild animals, seabirds and industrial processes (Sutton et al., 1995, 2000). Kapahi and Gross (1995) reported that bulk of ammonia emitted to the atmosphere results from anthropogenic activities since only 1 to 2 million tonnes per year (Bottger et al., 2001) of ammonia originates from natural sources.

Apart from ammonia being a non-point source (NPS) pollutant of water and soil systems, it can have a negative impact on the environment by forming secondary particulate matter when it reacts chemically with nitric and sulfuric acid in the atmosphere. These secondary particulate matter have drastic effects on human health and visibility (Heber et al., 2002) and therefore there is a lasting interest to search for ways to minimize the release of the gas into the environment. A feasible way to remove ammonia is the adsorption process. This is an effective method for gas emission control, especially for low concentrations (Heumann, 1997). Adsorption is a process that uses special solids (called adsorbents) to remove substances from either gaseous or liquid mixtures.

Industrial adsorbents that used to remove ammonia from air streams include activated carbon (Noll et al., 1992), zeolites, and ion-exchange resin. The expenses related to the development of these adsorbent are relatively high. Apart from the cost involved in developing these adsorbents they low adsorption capacity and the necessity of activating them before use makes the whole process non-economical. In view of the above drawbacks, therefore the need to develop an inexpensive material for removing and entrapping ammonia. This study proposes a simple technology for producing the adsorbent using an agricultural residue.

1.1 Research Objectives

The focus of this thesis is to develop and characterize corn cob, a biodegradable material for ammonia removal. A comprehensive review of the literature showed no published literature on the use of corn cob, (CC) for ammonia removal. Therefore the present investigation was initiated to investigate the ammonia removal properties of CC. The specific objectives are:

1. **Prepare a novel biodegradable material using steam explosion method**. The goal here was to pretreat corn cob under different severities of temperature and time. This treatment step was to impact acidic properties to the sample.

2. **Quantify ammonia removal capacity of the raw and steam exploded corn cob using a packed bed and batch reactor.** This was to investigate the ammonia removal capacity of the prepared samples at the various pretreatment levels and to also determine the optimal adsorption capacity.

3. **Enhancement of SECC with acidic salts at the optimal condition.** Acidic salts were added to the optimal condition determined in objective 2. The main purpose was to enhance the removal capacity of the steam exploded corn cob

4. **Investigate the type of the adsorption using FTIR and TGA-DSC**. The main interaction of steam exploded corn cob and ammonia was studied to determine whether the reaction is by chemisoption or by physisorption.

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CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter is a review of literature covering the main principles relevant to this work. The first section is a discussion on the various ammonia sources, characteristics of each source, and controlling strategies currently adopted to curb emissions. This is essential for understanding the enormity of the problem associated with ammonia emissions and how to design benign systems to solve the high levels of emissions. The second part focuses on the various potential materials that could be used in reducing ammonia emissions. Again, this is relevant in making decisions as to the best material based on the availability, cost and overall process design. The highlight of this segment will be on the utilization of agricultural residue to produce a biodegradable material that is effective as an adsorbent. The final section will discuss the underlying principles of adsorption, kinetics and the various factors that affect it.

2. 1 Ammonia Sources and Characteristics

It is estimated by the World Health Organization, WHO, that 4.6 million people die each year as a result of air pollution. Many of these mortalities are due to both primary and secondary pollutants produced through human activities. A recent study by the National Research Council (NRC, 2002) identified ammonia emissions as a major air quality concern at regional, national, and global levels.

Ammonia is ubiquitous and is present in the environment as a result of natural biological processes and industrial activities. About 99% of ammonia present in the atmosphere is released by the breakdown of organic waste matter (WHO, 1986). The environmental

sources include emission of industrially produced ammonia, release through agricultural fertilization, as well as coal gasification or liquefaction (WHO, 1986). Agricultural operations also account for a considerable amount of the anthropogenic ammonia emitted (Aneja et al., 2003; Arogo et al., 2006). This is heavily due to livestock operations and agricultural fertilizer losses. The majority of the ammonia emitted as a result of livestock production originates from cattle operations; however, poultry and swine operations also produce large quantities of ammonia.

The release of ammonia into the atmosphere has an impact on both human and animals. When ammonia is deposited onto the soil via acid rain, it is subsequently converted by bacteria into a nitrate ion, NO_3^- (Lekkerkerk et al., 1995). The process of converting ammonia deposited onto the soil to nitrate is referred to as nitrification. The nitrification process forms hydrogen ions which results in acidification of the soil, leaching of NO_3^- to groundwater, and possible loss of other plant nutrients (Asman et al., 1998). In addition to acidification, excess nitrogen (N) loading can lead to over enrichment of both land and water ecosystems. Furthermore, excess of N deposition can cause the above ground portion of the plant to grow rapidly, leaving the root system relatively smaller and weaker and more susceptible to disease and harsh weather conditions (Lekkerkerk et al., 1995). Figure 2.0 illustrates the sources of ammonia emission and it's impart on the environment.

Atmospheric Transport of Gases and particles

Deposition

Deposition

River and streams

Bay/Estuary

Algal blooms

Eutrophification

Oxygen depleted

Emissions

Mobile | Urban areas | Agriculture | Industrial power plant
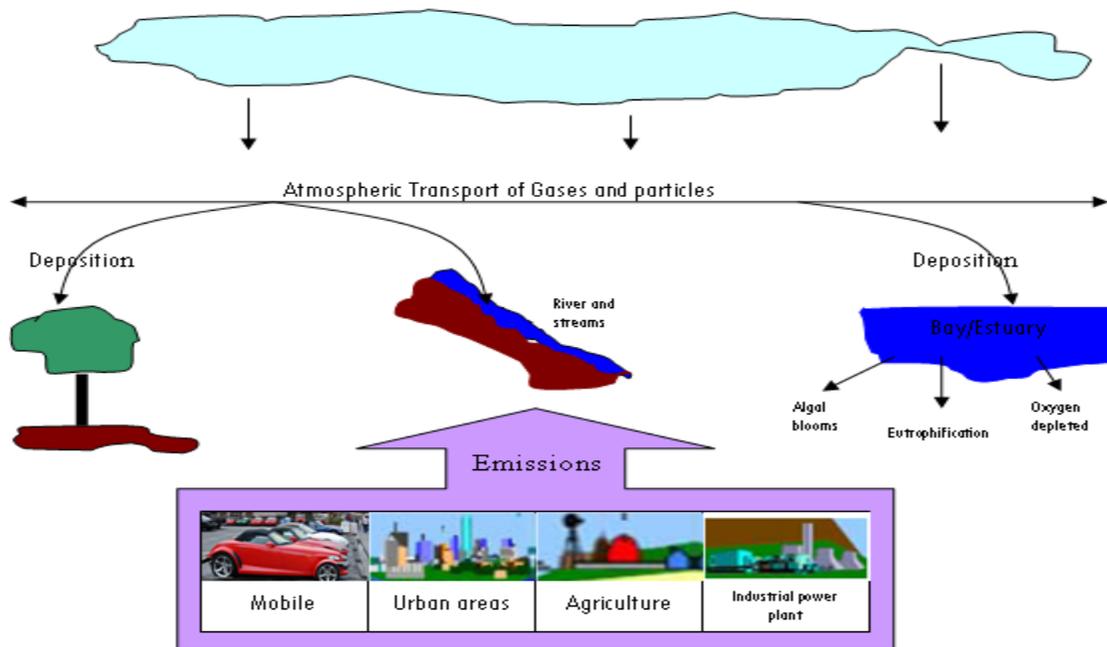
Figure 2.0 Illustration of the sources of ammonia emissions

In addition to its effects on water, plant, and soil systems, ammonia, which is the most abundant alkaline species in the atmosphere (Aneja et al., 2006), has the tendency to neutralize acidic gases such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x) (Asman et al., 1998). This results in the formation of particulate matter (PM) with a diameter of 2.5 microns or less, which is referred to as $PM_{2.5}$ (Makar et al., 2003; Gupta et al., 2003; Aneja et al., 2001; and Yamamoto et al., 1998).

$$NH_3\ (g) + HNO_3\ (g) \longleftrightarrow NH_4NO_3\ (s) \qquad (2.0)$$

$$NH_3\ (g) + H_2SO_4\ (g) \longleftrightarrow (NH_4)_2SO_4\ (s) \qquad (2.1)$$

This class of PM is of particular concern because the small size of the particles allows them to penetrate deep into the lungs. Several recent community health studies indicate that significant respiratory and cardiovascular problems are associated with exposure to $PM_{2.5}$ (Douglas, 2001), which leads to premature death and increased hospital admissions from respiratory causes. Children, the elderly, and individuals with compromised

cardiovascular health or lung diseases, such as emphysema and asthma, are especially vulnerable to such health problems caused by $PM_{2.5}$. These fine particles also contribute to the formation of haze. This is formed as a result of these fine particles encountering sunlight. According EPA (2004) reports, PM pollution is the major cause of reduced visibility (haze) in parts of the United States, including many of our treasured national parks and wilderness areas. Table 2.0 shows the health effect of these fine particles on humans.

Table 2.0 Health effects of Ammonia (Used with permission from Atta (2006))

Concentration (ppm)	Health Response
24 - 50	Nose and throat irritation after ten minutes of exposure
72 - 134	Irritation of nose and throat after five minutes exposure
700	Immediate and severe irritation of respiratory system
5000	Respiratory spasms, rapid suffocation
Above 10,000	Pulmonary edema, potentially fatal accumulation of fluid in lungs and death

Although ammonia at certain exposure limits is harmful, it is also beneficial to both human and plant. Ammonia gas is mainly used in the fertilizer industry as a raw material for the production of ammonium solution, nitrate and phosphate, calcium and sodium nitrate, ammonium sulfate, ammonium superphosphates and urea. This gas is also an important raw material in the manufacture of nitric acid, synthetic urea, plastics, rubbers, varnishes, fungicides, germicides, and disinfectants. It is employed as a coolant gas in

refrigeration systems, in the pharmaceutical, tanning, and mirror silvering industries, as well as in the manufacturing of military explosives (Gary, 2006).

2.2 Adsorbent and its Characteristics

Ammonia can be removed from air by adsorption process. This is normally achieved using an adsorbent. The adsorbent used for this process can be in the form of spherical pellets, rods, moldings or monoliths. The material must have high abrasion resistance, high thermal stability and small micropore diameter. The high microporosity of the material contributes to higher surface area and hence high capacity of adsorption. Also, the adsorbents must have a significant macropore structure to facilitate the fast transport of ammonia. The adsorbent can be classified as follows:

1. Oxygen- containing compounds – There are hydrophilic and polar e.g. silica gel and zeolite,

2. Carbon-based compounds – There are polar or non-polar e.g. activated carbon, and;

3. Polymer – based compounds – There are polar or non-polar functional groups in a porous polymer matrix e.g. ion exchange resins

2.2.1 Oxygen – containing Compounds

The adsorption action of these materials is due to the hydrophobic interaction of the adsorbed molecule and the adsorbent. Silica gel is a chemically inert substance, polar, and dimensionally stable amorphous form of SiO_2 (see Figure 2.1). This adsorbent is normally prepared by reacting sodium silicate with sulfuric acid, which is followed by a series after- treatment processes such as aging, pickling, etc. The after-treatment methods impact various pore size distributions on it surface. It is used for drying natural gas and

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adsorption of higher polar hydrocarbons from natural gas. Zeolite, another oxygen-containing compound is a naturally occurring three-dimensional; microporous hydrated aluminosilicate mineral characterized by high internal surface area and high cation exchange capacities. Figure 2.2 depicts the structure of zeolite. Zeolites have the general stoichiometric unit cell formula: $M_{x/m}[(AlO_2)_x(SiO_2)_y].zH_2O$. Where M is the cation with valence m, z is the number of water molecules in each unit cell, and x and y are integers such that $y/x \geq 1$. The cations balance the charge of the AlO_2 groups, each having a net charge of -1. They are made by hydrothermal synthesis of sodium aluminosilicate in an autoclave followed by ion exchange with cations such as Na^+, Li^+, Ca^{2+} and K^+. The above process is followed by drying and then pelletization. The adsorbent is activated at $650^\circ C$. These adsorbents contain very narrow pore size distributions offering highly selective physical properties. The properties and applications of five of the most commonly used molecular sieve zeolites are summarized in Table 2.1 below. The zeolite clinoptilolite has a specific affinity for ammonium ions and ammonia.
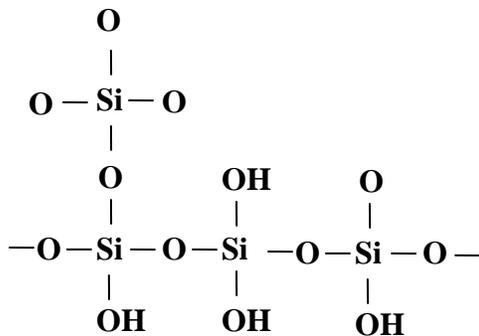
Figure 2.1 Structure of Silica gel   Figure 2.2 Structure of Zeolite
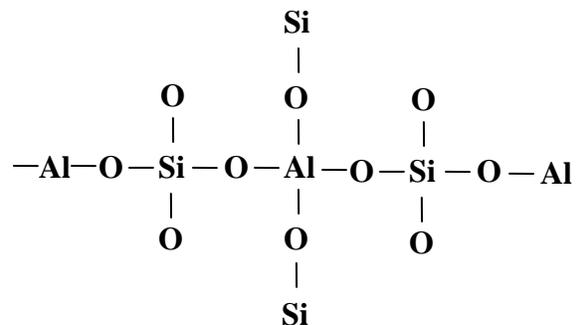
Table 2.1 Properties and Applications of Zeolites

Designation	Cation	Unit cell formula	Aperture size (nm)	Typical applications
3A	K^+	$K_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	0.29	Drying of reactive gases
4A	Na^+	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	0.38	H_2O, CO_2 removal; air separation
5A	Ca^{2+}	$Ca_5Na_2[(AlO_2)_{12}(SiO_2)_{12}]$	0.44	Separation of air; linear paraffins
10X	Ca^{2+}	$Ca_{43}[(AlO_2)_{86}(SiO_2)_{106}]$	0.80	Separation of air; removal of mercaptans
13X	Na^+	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$	0.84	

2.2.2 Carbon-based compounds

These are hydrophobic and non-polar compounds such as activated carbon. They are highly porous, amorphous solids consisting of microcrystallites with a graphite lattice (see figure 2.3). They have been the number one choice for treating flue gas. This is probably because of economics, particularly when the material will be used only once (i.e., with no regeneration). Some of their main drawbacks are that they are combustible and difficulty to completely regenerate.

The base materials for activated carbon manufacturing include: wood, coal, peat, coconut shells, recycled tires, and others. The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600°C in an oxygen-deficient atmosphere that cannot support combustion. The last stage is activation of the carbonized particle by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. Literature survey

indicates that there have been many attempts to obtain low-cost acitvated carbon or adsorbent from agricultural wastes. Table 2.2 shows various agricultural materials used for producing activated carbon and other adsorbents. This means that any cheap material, with high carbon content and low inorganics, can be used as a material for the production of activated carbon (Haykiri-Acma, Yaman and Kucukbayrak, 2005).

Skeleton of
Carbon

Pore
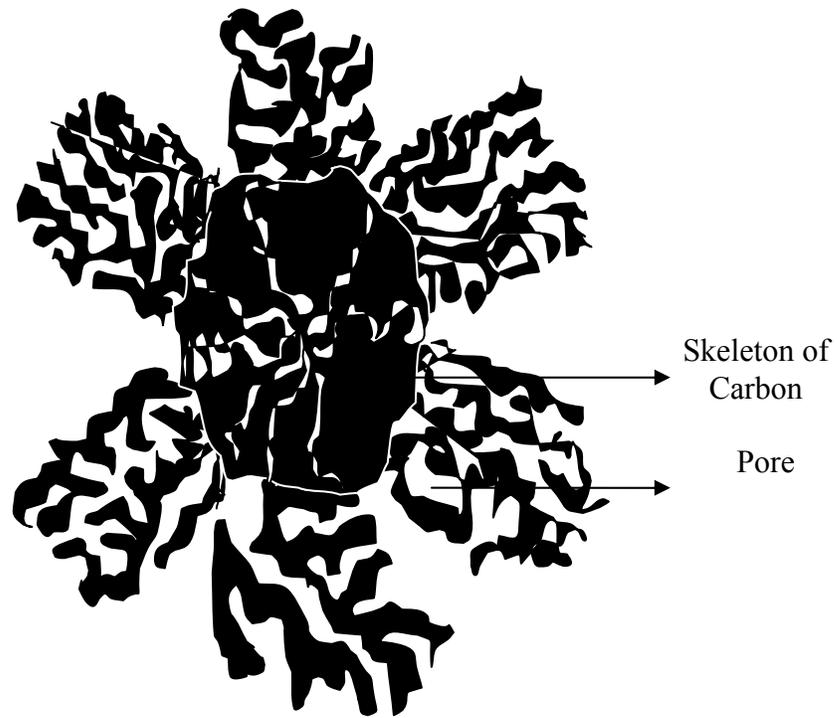
Figure 2.3 Structure of Activated carbon

Table 2.2 Agricultural residues used for production of adsorbents (Ioannidou and Zabaniotou, 2006)

Activation	Step of Process	Material
Physical	Two - steps	pistachio-nutshells, sunflower shells, pinecone, rapeseed, cotton residues, olive residues, peanut hulls, almond shells, oak, corn hulls, corn stover, rice straw, rice husk, rice hulls, pecan shells, sugarcane bagasse, olive-waste cakes
Chemical	One - step	corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells
Steam - Pyrolysis	One - step	Olive seeds, straw, birch, baggase, miscanthus, peanut hulls, corn stover, apricot stones, cherry stones

2.2.3 Polymer-based compounds

Polymer-based adsorbents are polar or non-polar functional groups in a porous polymer matrix. Examples of polymer-based adsorbents include modified celluloses (Miyata, 1987 & Okada et al., 1995) and ion exchange resins (Bolto and Pawlowski, 1987 & Noll et al., 1992). An ion exchange resins are an insoluble matrix (or support structure) normally in the form of small (1-2 mm diameter) beads, usually white or yellowish, fabricated from an organic polymer substrate. They have a highly developed structure pores on the surface of which are sites which trap and released ions. Ion exchange resins

are normally characterized into cationic or anionic types (see Figure 2.5 and 2.6). This type of adsorbent work by the trapping of ions with a simultaneous releasing of other ions; thus the process is called ion exchange.The most common synthetic structures are:

1. Cross-linked polystyrene

2. Cross-linked polymethacrylate

3. Phenol-formaldehyde

The polystyrene type is the most commonly used. Ion exchange resins are widely used in different separation, purification, and decontamination processes. The most common examples are water softening and water purification.
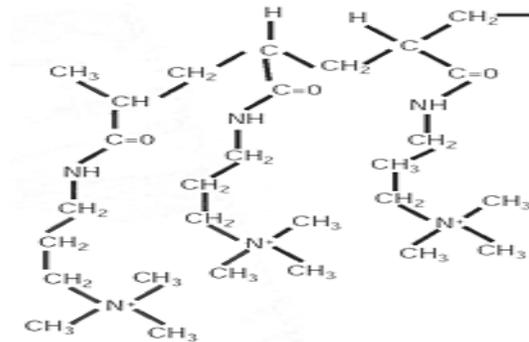
Figure 2.4 Strong base anionic resin polyacyrlic type
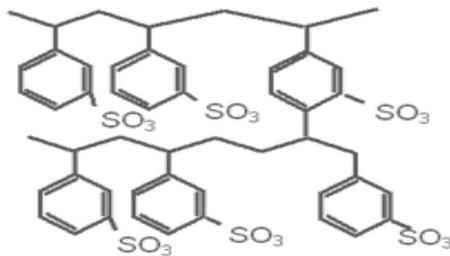
Figure 2.5 Strong acid cationic resin polystyrenic

2.3 Steam Explosion Adsorbent

Most adsorbents are manufactured at high temperatures. This makes the process energy intensive and therefore expensive thereby affecting the overall cost of reducing air pollution. Steam explosion, a method developed by W. H. Mason in 1925 is currently used to pretreat biomass for the production of biomolecules, chemicals and biofuels. According to Overend and Chornet (1988), steam explosion process is thermomechanochemical. The breakdown of structural components is assisted by heat in the form of steam (thermo), shear forces due to the expansion of moisture (mechano), and hydrolysis of glycosidic bonds (chemical).

Steam explosion can be carried out on a great variety of plant biomass including forest (Saddler et. al., 1993) and agricultural residues such as sugarcane (Dekker and Wallis, 1983) and cassava (Carta et al., 1999), corn residue (Ropars and Marchal, 1992), and cotton gin waste (Jeoh and Agblevor, 2001).

2.4 Steam explosion mechanism

Steam pretreatment in a batch reactor involves heating of biomass material at high temperatures and pressures, followed by mechanical disruption of the pretreated material either by violent discharge into a collecting tank (explosion) (Schwald et al., 1989) or by mild blending after bleeding the steam pressure down to atmospheric (no explosion) (Ramos et al., 1992). The high-pressure steam radically modifies the plant cell wall structure, yielding a dark brown material from which partially hydrolysed hemicelluloses are easily recovered by water-washing, leaving a water-insoluble fraction composed of cellulose, residual hemicelluloses and a chemically modified lignin.

During steam explosion high pressure steam condenses making the biomass material wet. The moisture in the biomass hydrolyzes the acetyl groups of the hemicelluloses fractions, forming organic acids such as acetic, uronic, formic and levulinic. The steam pretreatment is referred to as autohydrolysis since the breakdown of the glycosidic linkages are acid-catalyzed by resultant organic acids formed during the process. The extent of the breakdown of glycosidic linkages is primarily dependant upon acids that are released from the biomass itself. Also during steam explosion, lignin is primarily degraded through the homolytic cleavage of β-O-4 ether and other acid-labile linkages, producing a series of cinnamyl alcohols derivatives (Tanahashi et al., 1989) and condensation by-products. When the pressure is released, moisture within the biomass evaporates instantaneously become of the sudden decrease in pressure causing expansion of water vapor which exerts shear force on the surrounding structure. If the resultant shear force is high, it will cause mechanical breakdown of the lignocellulosic structure. Figure 2.6 illustrates the autohydrolysis of hardwood.
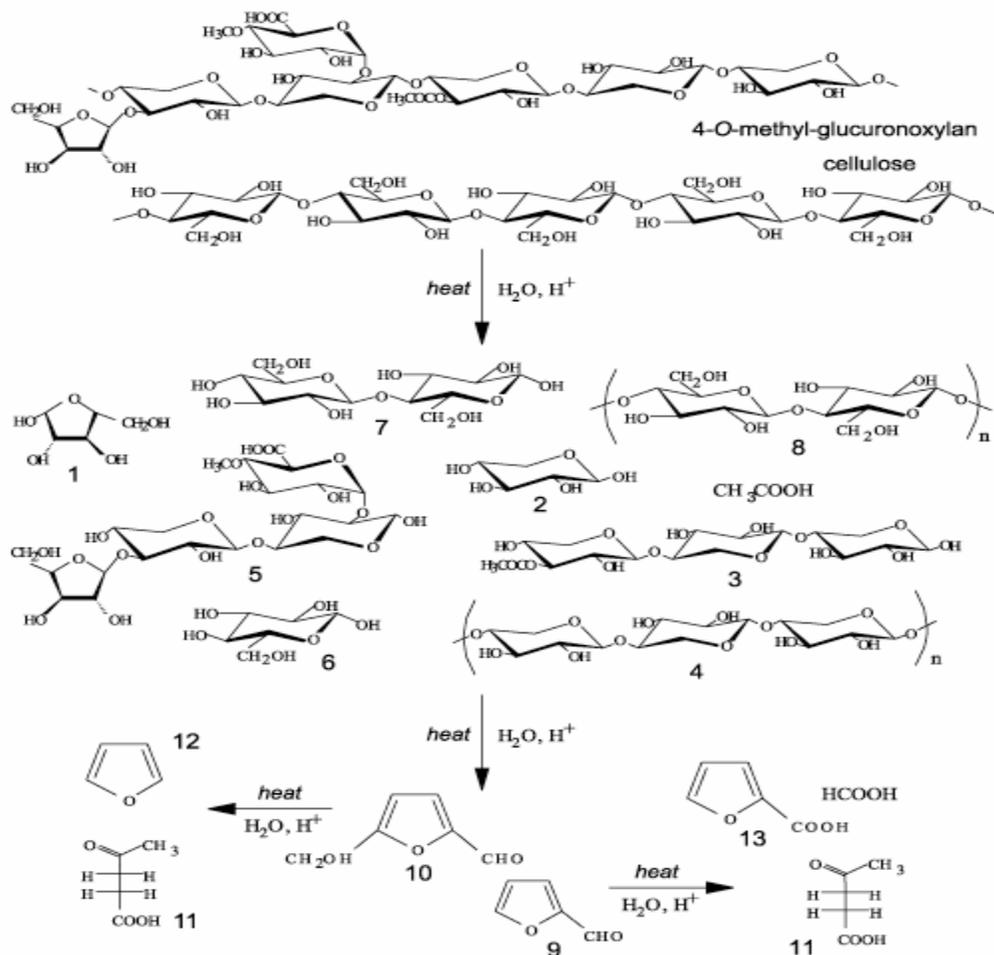
Figure 2.6 Hydrolysis of 4-O-methylglucuronoxylan and cellulose as result of steam explosion of hardwoods – Used with permission from Ramos (2003). (1) Arabinose; (2) Xylose; (3) Acetylated xylooligomers (DP of 3); (4) Xylooligomers of higher molecular mass; (5) Acetic, branched oligosaccharides; (6) Glucos; (7) Cellobiose; (8) Cellooligomers; (9) Furfural; (10) Hydroxymethylfurfural; (11) Levulinic acid; (12) Furan; (13) 2-furoic acid (pyromucic acid)

Adopted from Ramos (2003)

2.5 Adsorption Principles

When an adsorbable gas is brought into contact with a solid phase capable of adsorbing the gas on its surface, molecules are transferred from the gas to the solid phase. This

process takes place at a finite rate, which may correspond to the number of collisions of gas molecules with the adsorbent surface at the temperature and pressure specified. The rate is called the limiting rate. According to the kinetic theory of gases, the number of molecules, Z which collide per unit Area (A) on the surface in unit time is given by Equation (2.3):

$$Z = \frac{N_A P}{\sqrt{2\pi MRT}} \qquad (2.3)$$

Where N_A is Avogadro's number, M is Molecular weight of the gas, R is gas constant, P is pressure and T is temperature.

Adsorption occurs in a series of three steps. In the first step, the contaminant diffuses from the bulk gas stream to the external surface of the adsorbent material. In the second step, the contaminant molecule migrates from the relatively small area of the external surface (a few square meters per gram) to the macropores, transitional pores, and micropores within each adsorbent. Most adsorption occurs in the micropores because the majority of available surface area is there (hundreds of square meters per gram). In the final step, the contaminant molecule adheres to the surface of the pore. Figure 2.7 illustrates this overall diffusion and adsorption process. Steps 1 and 2 are diffusional processes that occur because of the concentration difference between the bulk gas stream and the film layers. Step 3 is the actual physical bonding between the molecule and the adsorbent surface. This step occurs more rapidly than steps 1 and 2.
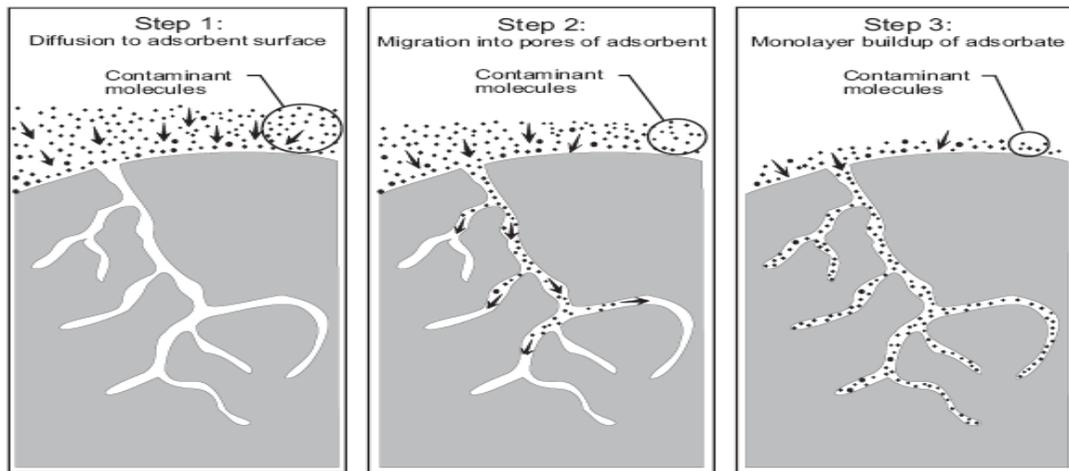
Figure 2.7 Adsorption steps

2.5.1 Adsorption Definitions

Since adsorption is a comparatively specialized technology, a capsule definition of terms may be helpful. Table 2.3 defines the various terminologies worth noting.

Table 2.3 Adsorption definitions

Terms	Definitions
Adsorbent	The surface of the solid material
Adsorbate	The gas or vapor contacting the adsorbent
Adsorptive	The gas or vapor in the bulk phase
Adsorption	The process describing the accumulation of material on the adsorbent surface
Desorption	The adsorbate in the condensed phase passes from the surface (of the adsorbent) to the fluid phase
Absorption	A process involving bulk penetration of gas into the structure of the solid (or liquid) which is usually associated with an increase in the bulk volume

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| Sorption | A process involving both **Ad**sorption and **Ab**sorption simultaneously |

2.6 Factors Affecting Adsorption

2.6.1 *Surface Area*

Surface area is one of the principal characteristics affecting the adsorptive capacity of an adsorbent, since the adsorption process results in a concentration of solutes at the surface. The Brunauer-Emmett-Teller (BET) method is the most widely used procedure for the determination of the surface area of solid materials (Jo´zsef et al.; 1999) and involves the use of the BET (Brunauer et al.; 1938) expressed as in Equation (2.4):

$$\frac{1}{w(\frac{p_o}{p}-1)} = \frac{1}{w_m C} + \frac{C-1}{w_m C}\left(\frac{p_o}{p}\right) \qquad (2.4)$$

Where:

W is the weight of gas adsorbed at a relative pressure P/P_o, and W_m is the weight of adsorbate constituting a monolayer of surface coverage. *C*, is the BET constant. The BET constant is related to the energy of adsorption in the monolayer and consequently its value is an indication of the magnitude of the adsorbent/adsorbate interactions. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

1. gas molecules physically adsorb on a solid in layers infinitely;

2. there is no interaction between each adsorption layer; and

3. the Langmuir theory can be applied to each layer.

The BET equation (2.4) requires a linear plot of 1/ [*W* (P_o/*P*)-1] vs. P/P_o which for most solids, using nitrogen as the adsorbate, is restricted to a limited region of the adsorption

isotherm, usually in the *P/P_o* range of 0.05 to 0.35. This linear region is shifted to lower

relative pressures for microporous materials. A typical BET plot is shown in Figure 2.8.
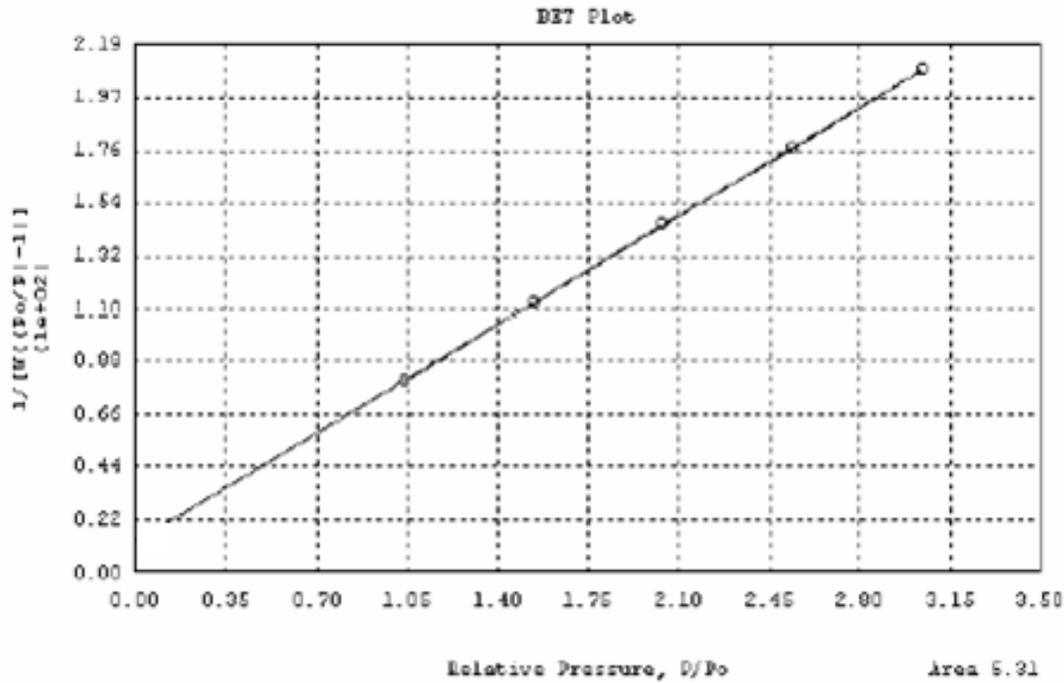
Figure 2.8 Typical BET plot

The normal multipoint BET procedure requires a minimum of three points in the

appropriated relative pressure range. The weight of a monolayer of adsorbate Wm can

then be obtained from the slope and intercept of the BET plot to give Equations 2.5 and

2.6 as shown below:

$$s = \frac{C-1}{w_m C} \qquad (2.5)$$

$$I = \frac{1}{w_m C} \qquad (2.6)$$

Where s and I are the slope and intercept of the BET plot respectively.

Thus, the weight of a monolayer W_m can be obtained by combining Equations 2.5 and 2.6 to give Equation 2.7.

$$W_m = \frac{1}{s+I} \qquad (2.7)$$

The next step in the application of the BET method is the calculation of the surface area. This requires knowledge of the molecular cross-sectional area A_{cs} of the adsorbate molecule. The total surface area S_T of the sample can be expressed as in Equation 2.8:

$$S_T = \frac{W_m N_A A_{cs}}{M} \qquad (2.8)$$

Where N is Avogadro's number (6.023 x 10^{23} molecules/mol) and M is the molecular weight of the adsorbate. Nitrogen is the most widely used gas for surface area determinations (Gregg et al.; 1982) since it exhibits intermediate values for the C constant (50-200) on most solid surfaces. Studies on the use of other gases such as argon (Corrin, 1951), krypton (Haul et al.; 1956) and xenon (Cochrane et al.; 1967) have been performed, but nitrogen remains the standard for surface area determination. The specific surface area S of the solid can be calculated from the total surface area S_T and the sample weight w, according to Equation (2.9):

$$S = \frac{S_T}{w} \qquad (2.9)$$

2.6.2 *Pore Structure*

A pore is a small opening in a solid substance of any kind that contributes to the substance's porosity. The International Union of Pure and Applied Chemistry (Sing et al.; 1985) has recommended a classification for porous materials where pores of less than 2 nm in diameter are termed "micropores", those with diameters between 2 and 50 nm are termed "mesopores", and those greater than 50 nm in diameter are termed "macropores".

Porosity of porous solids can be conveniently characterized by gas adsorption studies. Two common techniques for describing porosity are the determination of total pore volume and pore size distribution. For the evaluation of porosity of solid materials, nitrogen at 77K is the most suitable adsorbate.

2.6.3 *Total Pore Volume*

The total pore volume is derived from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate.

2.6.4 *Pore Size Distribution*

The distribution of the pore volume with respect to the pore size is called a pore size distribution. It is generally accepted that the desorption isotherm is more appropriate than the adsorption isotherm for evaluating the pore size distribution of an adsorbent. The reason being that desorption branch of the isotherm, for same the volume of gas, exhibits a lower relative pressure, resulting in a lower free energy state. Thus, the desorption isotherm is closer to true thermodynamic stability.

2.6.5 *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) by which the adsorbate molecules become physically fastened to the adsorbent molecules (Everett, 1971). 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 a new chemical compounds at the surface of the adsorbent, and energy would be necessary to reverse the process (Wedler, 1997). 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. Table 2.4 is a summary of the differences between chemisorption and physisorption.

In chemisorption, the heat of adsorption is comparable to the heat evolved from a chemical reaction, usually over 40 kJ/mol (Nollet et al., 2003). The heat given off by physical adsorption is much lower, approximately less than 40 kJ/mol, which is comparable to the heat of condensation. Molecules that are adsorbed by chemisorption are very difficult (and, in some cases, impossible) to remove from the adsorbent bed. Either increasing the operating temperature or reducing the pressure of the adsorbent bed can usually remove physically adsorbed molecules. Factors affecting adsorption according to Cheremisinoff (1993) 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 gas phase;

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

5. The residence time of the system

Table 2.4 Differences between chemisorption and physisorption adsorption

Physisorption	Chemisorption
Weak, reversible binding (via van der waals forces)	Strong, irreversible binding (via chemical bonds)
Occurs near or below adsorbate's critical temperature	Can occur far above adsorbate's critical temperature
Low heat of adsorption (close to heat of condensation)	High heat of adsorption (usually > 20 kcal/mol)
Non-activated (less adsorption at higher temperature)	May be activated
Multilayer adsorption	Monolayer adsorption
Non-specific	Specific with respect to surface characteristic

2.6.6 Nature of Adsorbate

The process of adsorption is spontaneous and is normally 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 adsorbate 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 Equation 2.10.

$$\Delta H = \Delta G + T\Delta S \qquad (2.10)$$

An increase in temperature therefore results in a reduction of the equilibrium adsorptive capacity (Cheremisinoff, 1993).

2.6.8 Adsorption Equilibria

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. This is an essential ingredient for the understanding of how much components can be accommodated by a solid adsorbent. This information can be used in the study of adsorption kinetics of a single component, adsorption equilibria of multicomponent systems, and then adsorption kinetics of multicomponent equilibria.

Several adsorption equilibria models have been documented in literature. Langmuir model is among the most widely used model. This model allows us to understand the monolayer surface adsorption on an ideal surface. Langmuir (1918) was the first to propose a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint. That is, there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium. The assumptions of the Langmuir models are:

1. Surface is homogenous, that is adsorption energy is constant over all sites

2. Adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites

3. Each site can accommodate only one molecule or atom

The Langmuir theory is based on a kinetic principle, that is the rate of adsorption (which is the striking rate at the surface multiplied by sticking coefficient) is equal to the rate of desorption from the surface.

The rate of striking the surface, in mole per unit time and unit area, obtained from the kinetic theory of gas is given by Equation 2.3.

For example the magnitude of this bombardment rate of ammonia molecule at three different pressures is showed in Table 2.5 below:

Table 2.5 Rate of collision of molecule with pressure

Pressure, Torr	Z, molecules/(cm^2sec)
760	3.0 x 10^{23}
1	4.0 x 10^{20}
1.0 x 10^{-3}	4.0 x 10^{17}

This shows a massive amount of collision between the molecule and the surface even at a pressure of 1 x 10^{-3} torr.

During adsorption, when the adsorbable gas strikes the surface of the adsorbent, some fraction will condense and is held by the surface force until these adsorbed molecules evaporate again (Figure 2.10). Langmuir (1918) noted that for an ideal surface this fraction is unity, but for a real surface which is usually far from ideal this could be much less than unity.
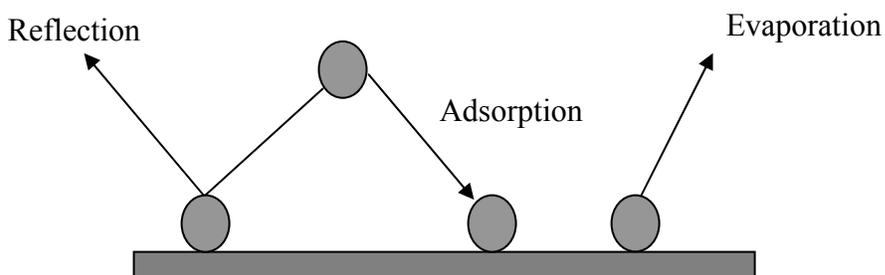
Figure 2.10 Schematic diagram of Langmuir Adsorption on flat surface

The rate of adsorption for a real surface is modified by α, the sticking coefficient (which accounts for non perfect sticking) is given by Equation 2.11.

$$Z = \frac{\alpha N_A P}{\sqrt{2\pi MRT}} \qquad (2.11)$$

This is the rate of adsorption on a bare surface. On an occupied surface, when a molecule strikes the portion already occupied with an adsorbed species, it will evaporate very quickly, just like a reflection from a mirror. Therefore, the rate of adsorption on an occupied surface is equal to the striking rate given equation (2.3) multiplied by the fraction of empty sites, to give Equation 2.13.

$$Z_a = \frac{N_A P}{\sqrt{2\pi MRT}}(1-\theta) \qquad (2.12)$$

where Θ is the fractional coverage.

The rate of adsorption usually decreases with increasing extent of adsorption. The rate of adsorption according to Masel (1996) may be limited by:

1. the rate of mass transfer of the gas to the adsorbent surface (convection and external diffusion);

2. the rate of mass transfer within pores in the adsorbent (internal diffusion);

3. the rate of transfer of heat liberated by the adsorption process from the captured molecule to the adsorbent;

4. the surface migration rate, is in principle, the rate of activation migration of the adsorbed molecules favorable for adsorption and;

5. the rate of the surface process, requiring for example, that an activation energy be supplied; and

6. by the fact that adsorption may change into a volume reaction which is not solely limited to the adsorbent surface.

The rate of desorption from the surface is equal to the rate, which corresponds to fully covered surface (k_d), multiplied by the fractional coverage, given in Equation 2.13.

$$Z_d = k_d \theta \qquad (2.13)$$

Adsorption involves the concentration of the gas on the surface. As the adsorption process proceeds, equal amounts of solute are being eventually adsorbed and desorbed simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state. The position of equilibrium is characteristic of the gas concentration, adsorbent, and temperature (József, 2002).

2.7 Adsorption Isotherm

An understanding of the surface area and porosity of an adsorbent can be achieved by the construction of an adsorption isotherm. When the quantity of adsorbate on a surface is measured over a wide range of relative pressures at constant temperature, the result is an adsorption isotherm.   IUPAC in 1994 extended the original adsorption isotherm classification proposed by Brunauer, Deming, Deming and Teller (Brunaur et al., 1940) to give six generic adsorption isotherms, as shown in Figure 2.11.
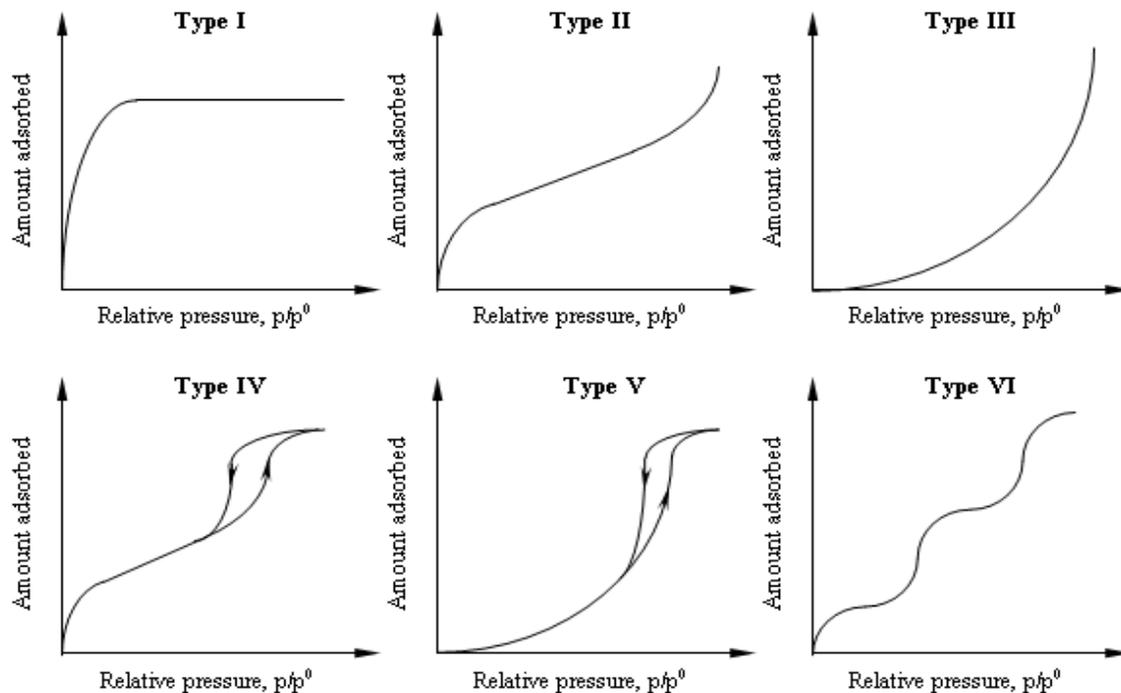
Figure 2.11 IUPAC Classification of adsorption Isotherm

The type I or Langmuir isotherms are concave to the P/P_0 axis and the amount of adsorbate approaches a limiting value as P/P_0 approaches 1. Type I physisorption isotherms are exhibited by microporous solids having relatively small external surfaces, for example, activated carbons and molecular sieve zeolites. The limiting uptake of adsorbate is governed by the accessible micropore volume rather than by the internal surface area. Whilst the type I isotherm are exhibited by microporous solids, type II isotherm are used to describe nonporous or macroporous solids. This type of isotherm represents unrestricted monolayer-multilayer adsorption.

Type III isotherms are convex to the P/P_0 axis over its entire range. This type of isotherm is rarely encountered. A well-known example is the adsorption of water vapor on non porous carbons. The type of isotherm associated with capillary condensation in mesopores is type IV. The capillary condensation is indicated by the steep slope at higher

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relative pressures. The initial part of the type IV isotherm follows the same path as the type II. Type V isotherms are uncommon, corresponding to the type III, except that pores in the mesopore range are present.

Types I, II and III adsorption isotherms are generally reversible, but microporous materials having type I isotherms can exhibit hysteresis. Types IV and V, associated with mesoporosity, usually exhibit hysteresis between the adsorption and desorption isotherms.

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CHAPTER THREE

AMMONIA ABSORPTION BY STEAM EXPLODED CORN COB

ABSTRACT

A novel biodegradable ammonia control material was developed from steam exploded corn cob. The effect of steam explosion severity (2.94, 3.32, 3.42, 3.64, 3.80, 3.83, 4.02, 4.10, 4.17 and 4.32) on the ammonia absorption capacity of the biodegradable material was investigated using packed column and titration of slurries prepared from water. The packed column studies showed that the maximum absorption capacities of the raw corn cob (RCC) and the steam exploded corn cob (SECC) were respectively 10.45 mg NH_3/g RCC and 59.80 mg NH_3/g SECC. However, the titration of the slurries with a base showed that the capacity of the SECC was 14.4 times that of RCC. The large difference between the packed column (SECC/RCC = 5.7) and the slurry titration (SECC/RCC = 14.4) was probably because: (1) the initial ammonia reaction products blocked the pores of the SECC and reduced diffusion into the pore structure; (2) the ammonia gas flow rates were too high and therefore the gas did not penetrate the pores; (3) the gas contact time was below the equilibrium value; and (4) since interior pore surface area is usually larger than the external surface area of a particle, it appears the low column SECC/RCC ratio is due to reactions on the SECC particle surface whereas the slurry result was a combination of both. The simple addition of small quantities of $Al_2(SO_4)_3 \cdot xH_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ to SECC improved the acidity of the mixture, whereas the impregnation of the SECC with $Al_2(SO_4)_3 \cdot xH_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ reduced the acidity of SECC and its ammonia removal capacity.

Keywords: Corn cobs, absorption, Adsorption, Steam explosion, Severity factor

3.0 Introduction

Recent advances in the understanding of the health impacts of particulate pollution and the important role ammonia (NH_3) emissions play in the formation of secondary particulate matter (PM) has generated new research interest in ammonia emissions. Major sources of NH_3 emissions include livestock operations, fertilizer use, waste management, mobile sources, industrial point sources, and various biological sources including human respiration, wild animals, and soil microbial processes. It is estimated that the total amount of ammonia emitted annually is $113-244 \times 10^6$ (WHO, 1986). Thus, the development of improved methods to mitigate the high levels of the gas is required.

Ammonia has pungent, acrid odor at concentrations greater than 0.7 ppm and it is an irritant. Concentrations of 50-150 ppm can lead to a severe cough and mucous production (Leduce, et al., 1992). In addition to pulmonary disease, exposure to ammonia leads to irritation of eyes, sinuses, and skin (Latenser et al., 2000). Major impacts associated with atmospheric ammonia and their depositions included soil acidification, eutrophication, and aerosol formation. It is therefore imperative to develop benign processes to reduce the emission of the gas into the environment. The present work investigated the control of the emission of ammonia through adsorption by steam exploded corn cob.

Adsorption is an effective method for gas emission control, especially for low concentrations (Heumann, 1997). Adsorption is a process that uses special solids (called adsorbents) to remove substances from either gaseous or liquid mixtures. Many factors can affect the adsorption capacity of the adsorbent; these include the specific surface area, pore size distribution, pore volume, and surface functional groups (Chiang et al., 1999). Generally, the adsorption capacity increases with the specific surface area due to

the great number of adsorption sites (Gregg and Sing, 1982; Cheremisinoff and Ellerbursch, 1978). The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they have large surface areas per unit weight. Activated carbon is the most versatile adsorbent used for the removal of scent, taste, and color due to the presence of pollutants in gaseous or liquid mixtures (Noll et al., 1992). A number of processes for ammonia removal using activated carbon have been reported by Leuch and Bandosz, 2006, Turner et al. (1994), Rodrigues et al (2006), Saiki et al. (1994), El-Nabarawy et al. (1997), and Rodrigues et al. (1999).

Zeolites are aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally Na^+, K^+, Ca^{2+}, and Mg^{2+}) in addition to water in their structural framework that can be used to remove ammonia. The physical structure is porous, containing interconnected cavities in which the metal ions and water molecules are contained. Ammonia removal by ion-exchange has been investigated by many researchers such as Koon and Kaufman, 1975; Gaspard et al. 1983; Schoeman et al., 1986; Haralabous et al. 1992 and Melenov´a et al., 2002). Table 3.0 shows different adsorbent and their ammonia adsorption capacities.

Table 3.0 Ammonia adsorption capacity of some adsorbents					
Sample	Source	Condition		Adsorption capacity, $(mgNH_3/g)$	References
		Concentration (ppm)	Temperature, (^{o}C)		
Activated Carbon	coconut	600-2400	40	0.60-1.80	Rodrigues et al., 2006
		6000-2400	80	0.20-0.70	
		6000-2400	120	0.15-0.35	
Activated Carbon	Wood	100	25	3.90	Leuch and Bandosz (2006)
	Coconut	100	25	0.40	
	coal	100	25	0.90	
Activated carbon fiber	Phenol-formaldehyde resin	900	25	0.98	Christian et al., 1999
Natural Clinoptiole		350	25	12.20	Karel et al., 2006
	Impregnated with H_2SO_4	350	25	31.50	
13X-Molecular sieve		350	25	31.00[a]	Gurdeep and Prasad (1997)
5A Molecular sieve		350	25	14.00[a]	

Note: a – $mgNH_4^+/gSample$

In recent times the focus has been on the use of agricultural residue as adsorbent. Literature survey indicates that there have been many attempts to obtain low-cost

activated carbon or adsorbent from agricultural wastes such as wheat, corn straw, olive stone, birch wood, sunflower shell, corn stover, corn cob etc. See Table 2.2 for list of various agricultural residues currently used for the production of low cost adsorbent.

The preparation of most of these adsorbents, especially activated carbons involves two processes through physical and chemical activation (Lussier and Miller, 1994). Physical process involves carbonization of a carbonaceous material followed by the activation of the resulting char at a temperature between 800 and 1100 $^{\circ}$C in the presence of suitable oxidizing gases such as carbon dioxide or steam. In chemical process the precursor is mixed with a chemical agent and then pyrolyzed between 400 and 600 $^{\circ}$C in the absence of air. Chemical process offers several advantages in that it is carried out in a single step combining carbonization and activation, performed at lower temperatures and results in the development of a better porous structure. Environmental concerns of using chemical agents for activation is currently been looked being reexamined. To obtain adsorbent from these materials is expensive hence the use of steam explosion method is an attractive since the process is environmentally friendly.

Steam explosion combines three different processes (mechanical, thermal and chemical) to breakdown structural components of biomass. It is assisted by heat in the form of steam (thermal), shear forces due to the expansion of moisture (mechanical), and hydrolysis of glycosidic bonds (chemical). See sections 2.4 and 2.5 for more details on steam explosion.

The important variables in steam-explosion pretreatment are time, temperature, chip size, and moisture content (Saddler et. al., 1993). The effects of time and temperature/pressure of the treatment process can be represented by the severity parameter as defined by

Overend and Chornet (1987). The parameter combines time, t (min), and temperature, T (°C) in the form of:

$$R = \int_0^t e^{\left(\frac{T-100}{14.7}\right)} dt \qquad (3.1)$$

$$LogR = R_o = \text{severity parameter} \qquad (3.2)$$

Steam explosion offers several advantages compared with other biomass fractionation methods. These include the potential for significantly lower environmental impact, lower capital investment, potential for energy efficiency, less hazardous process chemicals and conditions, and the more complete recovery of all wood biopolymers in a usable form (Focher et al., 1991).

The main focus of this study was to develop a novel biodegradable material from corn cob using steam explosion concept. This pretreatment will impact both acidic properties and enhance the micro structure of the corn cob thereby making it efficient for the removal of ammonia. The corn cob is the hard thick cylindrical central core on which are borne the grains or kernels of an ear of corn. It is the by-product generated after separating the grains during the processing of corn. Corn is the most widely grown crops in the world and it was estimated that the total yield of corn rose from 35 million bushels in 1980 to a projected 2.15 billion bushels in 2006/07 (Linwood et al., 2007). The United States is the largest producer of corn in the world, averaging 279.5 million metric tons in 2003/04-2005/06, representing about 41 percent of global production. Since the ratio between corn grain and corn cobs may reach 100:18 (Qing et al., 2006), large quantities of corn cobs are generated. This huge amount of corn cob generated according to Lin et al., (1995) is classified as waste (. They are currently either used as animal feed or are

returned to the harvested field for land application. One form of getting rid of the waste is by conversion into energy by combustion. However, this method will generate serious problem of air pollution from burning. Recent development shows the possible utilization of this waste material into useful and valuable products.

Corn cobs contain approximately 391 g of cellulose, 421 g of hemicelluloses, 91 g of lignin, 17 g of protein, and 12 g of ash per kg of dry matter that can serve as a potential source of renewable biomass for the production of soluble sugars, ethanol and other valuable products by chemical, enzymatic, and microbial fermentation processes (Barl et al., 1991). Zdena et al. (1999) extracted the xylan from corn cobs which are used as additive in papermaking, textile printing and the pharmaceutical industry. Rivas et al. (2002) prepared the fermentable hydrolysate from corn cob. Ke-Chang (2004) investigated the behaviors of pyrolysis of corn cobs as energy source in a fixed bed reactor. Perotti and Molina (1988) also used corn cobs as a bacterial substrate for the production of forage protein. The preparations of activated carbon from corn cob by combination of chemical and physical activation (Tsai et al., 1998, 2001; Aggarwal and Dollimore, 1997) has been investigated but the use of steam exploded corn cob as adsorbent has not been reported in literature.

The use of this carbon-containing biomass in reducing ammonia can be a two-fold solution to environmental problems. It reduces the volume of the wastes and an increasing demand for abatement of ammonia emission might be fulfilled at a reasonable cost. Another advantage in application of these adsorbents is that there may be no need to regenerate them because of their low production costs. Therefore the goal of this study is

to investigate the effect of severity of steam explosion of corn cob on its capacity to remove ammonia.

3.1 Experimental Section

3.1.1 Materials and Apparatus

A 99.5% anhydrous ammonia (Airgas Inc, Radford, VA USA) was used as gas for this study. The experimental apparatus was a custom made packed bed reactor (60mm in diameter and 600mm in height) with embedded type J-thermocouple (OMEGA Engineering Inc, Stamford, CT, USA). The packed bed reactor (Figure 3.0) was insulated to prevent heat loss. A GFM17 mass flow meter (Aalborg Industries Inc, Carson CA, USA) was used to monitor the flow of ammonia gas during the experiment. The pH of both the RCC and SECC was measured using a corning pH meter (Model 440, Krackeler Scientific Inc, Albany, NY). A Metrohm Titrino 798 titrator (Brinkmann Instruments, Westbury, NY, USA) was used for the acid-base titrations.
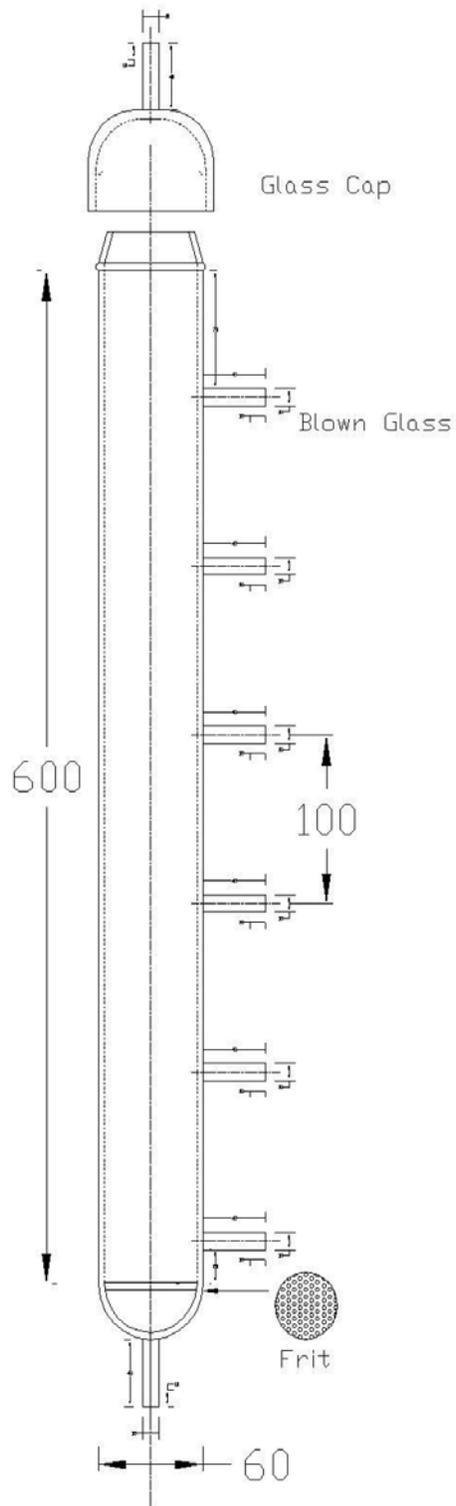
Figure 3.0 Custom made packed bed reactor. All dimensions are in mm

3.1.2 Methods

3.1.2.1 Preparation of adsorbent

The steam exploded corn cob was prepared in a 25-liter batch reactor located at the Thomas M. Brooks Forest Products Center (Virginia Tech). A 1000g batch of raw corn cob was steam exploded at various temperatures (200°C, 213°C, and 220°C) and various residence times (60, 180, and 300 seconds). For each experiment, the reactor was filled with 1000g of as received corn cob and the reactor sealed. Steam was then admitted into the reaction chamber and the temperature of the reactants was raised to the desired value. As soon as the desired temperature was attained the time of the reaction was started using a stop watch. At the end of the reaction time, the steam pressure was released by opening the valve at the bottom of the reactor (Figure 3.1). The steamed material was discharged through a cyclone and the mixture was collected in a stainless steel collection tank. The steam exploded corn cob (SECC) was air-dried at ambient laboratory conditions. The particle size of the dried material was determined by sieve analysis. Nine standard testing sieves (Soiltest Inc, Evanston, IL) of size (0.076, 0.106, 0.150, 0.180, 0.335, 0.420, 0.500, 1.000 and 2.000mm opening) were stacked on each other and sieved with Retsch sieve shaker (200 Basic, Retsch In, USA) for 15 min. The fractions were then weighed and the data used to determine the particle size distribution.
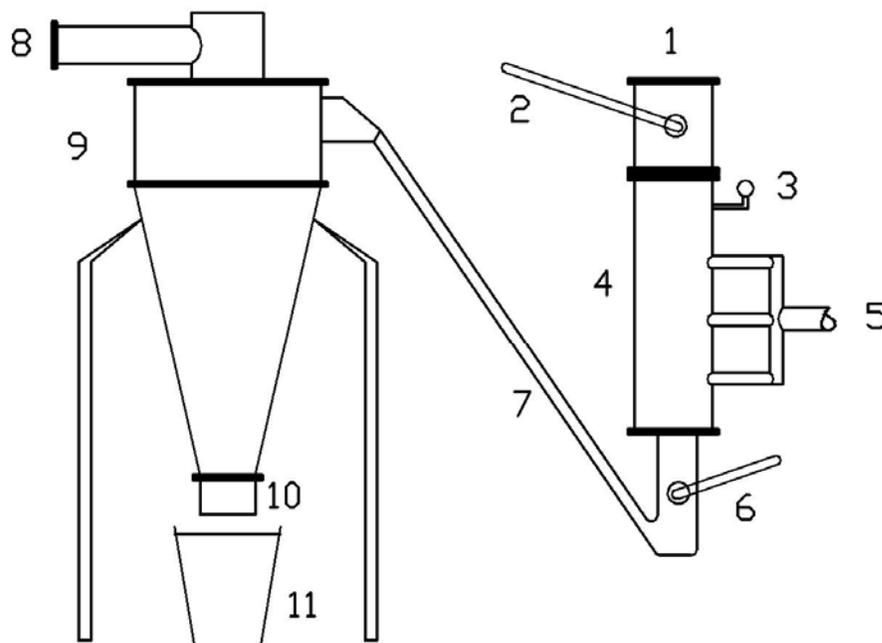
Figure 3.1 Schematic diagram of the Batch Steam Explosion Unit (1 – Feed inlet, 2 – Sample charging valve, 3 –Temperature gauge, 4 – Reactor body, 5 – Saturated Steam supply valve, 6 – Discharge valve, 7- Connecting Pipe, 8-Vent to Atmosphere, 9- Cyclone body, 10 - Cyclone outlet, and 11 – Collection bin).

3.1.2.2 Measurement of Physical Properties of steam exploded corn cob

3.1.2.2.1 *Total Surface area*

The nitrogen adsorption/desorption isotherms were used to determine the specific surface area, the specific pore volume and the pore size distribution of the samples in the mesopore range. The isotherms were measured at the boiling point of liquid nitrogen

using an AUTOSORB-I (Quantachrome, Syosset, NY) computer controlled automatic surface analyzer and data processing system. The specific surface area was calculated according to the multi-point B.E.T. method. The total pore volume was derived from the amount of vapor adsorbed at a relative pressure close to unity, assuming, that the pores were filled with liquid nitrogen. The pore size distribution was computed using the method proposed by Barrett et al. (1951). The t-method of Halsey (1948) was used for the determination of micropore volume in the presence of mesopores.

3.1.2.2.2 *Bulk Density*

The bulk density was measured using the method of Ahmedna et al. (1997), by placing (0.5-1.0 mm) size of SECC in a weighed 25 ml cylinder. After filling the measuring cylinder to the 25ml mark with the SECC material, the measuring cylinder and its content were weighed again. The difference between the weight of measuring cylinder and its content and weight of measuring cylinder is the weight of the dry sample. Knowing the weight of the dry sample and given that the SECC particles were filled to the 25 mL (volume of the packed dry sample) the bulk density was calculated using Equation 3.3.

$$\text{Bulk density (g/cm}^3) = \frac{\text{weight of dry sample (g)}}{\text{volume of packed dry sample (cm}^3)} \quad (3.3)$$

3.1.2.2.3 *Particle Density*

The particle density focuses on just the SECC material and not the total volume that the steam exploded corn cob particles and pore spaces occupy. A batch of 25.0 g (M_1) of SECC was weighed into a weighed 100 ml flask. 50ml of distilled water was added and the content weighed again (M_2). The SECC and water mixture was boiled for 10 minutes to remove air bubble and the mixture flask was closed and cooled for 24 hours. The volume of the flask was brought to the 100 ml mark and the content weighed again (M_3).

The volume of the particle with air removed was found as the difference between M_2 and M_3 multiplied by the density of water (1.0 g/cm^3). The particle density is found using Equation 3.4.

$$\text{Particle density (g/cm}^3) = \frac{\text{weight of dry sample (g)}}{\text{volume of sample only with air removed (cm}^3)} \quad (3.4)$$

3.1.3 Chemical Properties of steam exploded corn cob

3.1.3.1 *Ash Content*

The ash content of steam exploded corn was determined using the ASTM E 1756-2001 standard method. Thus, 1.0g of SECC was weighed into a pre-weighed porcelain crucible after determining its moisture content. The crucible and its content was ashed at 575°C for 8 h in a Thermolyne 1400 muffle furnace (Barnstead International, Dubuque, Iowa, USA).The crucible was then removed and placed in a dessicator and weighed after cooling. The ash content on moisture free basis was calculated using Equations 3.5 and 3.6

$$\text{Total solids content (\%)} = 100 - \text{Moisture Content (\%)} \quad (3.5)$$

$$\text{Ash (\%)} = \frac{\text{ash wt (g)}}{\text{Initial solids wt (g)} \times \text{Total solids content (\%)}} \times 100 \quad (3.6)$$

3.1.3.2 *Acidity*

The pH of steam exploded corn cob sample provides information about the average acidity or basicity of the material. A sample of 1.0g of dry steam exploded corn cob was added to 100ml of deionized water and the suspension was stirred for 2 hours at 25 °C to reach equilibrium. Then the sample was filtered and the pH of solution was measured using F-55500-10 Accumet (Cole-Parmer Instrument Company, Vernon Hills, Illinois, USA) pH probe.

3.1.4 *Titration of SECC slurries*

A 5.0 g batch of particle sizes of 0.5 to 1.0 mm of RCC and SECC were suspended in 50 ml of deionized water. The mixtures were titrated with 0.05 M NH_4OH using phenolphthalein indicator for end point determination.

A second set of experiments were conducted using a mixture of acidic salts and SECC. Weighed samples of aluminum sulfate hydrate, $Al_2(SO_4)_3.xH_2O$ and iron sulfate hydrate $Fe_2(SO_4)_3.xH_2O$ were added to the SECC to achieve fixed ratios (salts: SECC = 1:99, 2:98, 3:97, 5:95 and 9:91). The mixtures were slurried with 50mL deionized water and titrated with 0.05M NH_4OH using phenolphthalein as indicator for end point determination.

3.1.5 Augmentation of Steam exploded corn cob with acidic salts

In order to improve the adsorption capacities of the steam exploded corn cob, the samples were impregnated with acidic salts such as aluminum sulfate hydrate, $Al_2(SO_4)_3.xH_2O$ and iron sulfate hydrate, $Fe_2(SO_4)_3.xH_2O$. Samples of SECC and salt (ratio of salt to steam exploded corn cob were 1:99, 3:97, 5:95 and 9:91) were placed in 500 mL flask and 50 mL of deionized water added. The samples were placed in a water bath at 50 ^oC for 24 hours after which they were air dried at ambient conditions. The air-dried samples were also used in the packed bed experiments

3.1.6 Procedure for Adsorption Experiment

The experimental set up for the packed column experiment is shown in Figure 3.2

Figure 3.2 Experimental set up of ammonia adsorption in a packed bed reactor

A blank determination was first carried out by passing ammonia through the empty bed into a solution of 500mL cold boric acid for 5 min. The following reaction took place between ammonia and boric acid (Equation 3.7):

$$H_3BO_{3(l)} + NH_3 \rightarrow NH_4H_2BO_{3(l)} \tag{3.7}$$

The resultant $NH_4H_2BO_3$ solution was colorless, turning brownish after the addition of a 1% bromocresol green and methyl red indicator. The above solution was then titrated with 1 M hydrochloric acid (HCl) until it turned green at the end point. The reaction that occurred is shwon in Equation 3.8.

$$NH_4H_2BO_{3(l)} + HCl_{(l)} \rightarrow H_3BO_{3(l)} + NH_4Cl_{(l)} \tag{3.8}$$

Thus, the $NH_4H_2BO_3$ concentration can be calculated using Equation 3.9.

$$V_{NH_4H_2BO_3} \times M_{NH_4H_2BO_3} = V_{HCl} \times M_{HCl} \tag{3.9}$$

Where $V_{NH_4H_2BO_3}$ = Volume of ammonia borate

$M_{NH_4H_2BO_3}$ = Molarity of ammonium borate

V_{HCl} = Volume of hydrochloric acid

M_{HCl} = Molarity of hydrochloric acid

The mass of ammonia was determined from the Equation 3.10

: $$m_{NH_3} = M_{NH_4H_2BO_3} \times V_{NH_4H_2BO_3} \times M_{NH_3} \qquad (3.10)$$

Where m_{NH_3} = ammonia mass

M_{NH_3} = molecular weight of ammonia

3.1.7 Ammonia breakthrough capacity

About 50g of SECC was loaded into the packed bed reactor and weighed. Ammonia at a flow rate of 0.30 L/min was passed through the bed into the boric acid solution. Samples of boric acid solution were taken at 5 min intervals for the first 20 min and then at 10 min intervals for the next 20 min and then at 20 min intervals until the bed was saturated. The aliquots were titrated with HCl as described above.

After the bed reached saturation, the experiment was stopped and the reactor and its content were weighed again. Afterwards, a new set of experiment was started with the other samples.

Mass of incoming adsorbate up to time *t* is found using Equation 3.11.

$$M_{in} = QC_o \int_0^t dt = QC_o t \qquad (3.11)$$

Mass of outgoing adsorbate up to time t is given by Equation 3.12:

$$M_{out} = Q \int_o^t C dt = QC_o \int_o^t \frac{C}{C_o} dt \qquad (3.12)$$

The adsorbed mass is calculated using Equation 3.13 or with Equation 3.14.

$$M_{ads} = M_{in} - M_{out} \qquad (3.13)$$

$$M_{ads} = QC_o \int_o^t (1 - \frac{C}{C_o}) dt \qquad (3.14)$$

where Q is the flow (mL/min), C_o, the initial concentration of ammonia, C, the concentration of outgoing ammonia and M_{ads} adsorbed mass (mg/g).

3.2 Results and Discussions

The steam explosion process had a dramatic effect on the corn cob as shown in Figure 3.3. After steam explosion, the corn cob was reduced into coarse brown powder depending on the severity of the steam explosion. The higher the severity, the finer the particle size distribution. At very low severities, the corn cob was extremely coarse and could not be used for these studies.

(a) Raw corn cob   (b) Steam exploded corn cob

Figure 3.3 Starting materials and products after steam explosion.

The results from the sieve analysis (Tables 3.1 and 3.2) clearly showed that steam exploding RCC at high severities gave a finer product whilst low severities produced a coarse material. Figures 3.9 and 3.10 represent the particle size distribution of SECC at 200°C and 213°C respectively. The effect of severity on the particle size of SECC

becomes less pronounced at higher temperatures and reaction times. At higher severities the majority of SECC particles have a diameter around 0.5 – 2.00 mm.

Table 3.1 Sieve analysis of SECC at 200 $^{\circ}$C

Sieve operture, mm	SECC at 200 $^{\circ}$C for 1 min		SECC at 200 $^{\circ}$C for 3 min		SECC at 200 $^{\circ}$C for 5 min	
	percent of mass retained, %	Cumulative percent, %	percent of mass retained, %	Cumulative percent, %	percent of mass retained, %	Cumulative percent, %
0.00	1.32	1.32	1.11	1.11	2.31	2.31
0.08	0.08	1.40	0	1.11	0.14	2.45
0.11	0.13	1.53	0.37	1.48	0.90	3.35
0.15	0.14	1.67	0.35	1.83	0.92	4.27
0.18	0.45	2.12	2.11	3.94	6.24	10.51
0.36	0.52	2.64	2.07	6.01	4.84	15.35
0.42	0.24	2.88	0.26	6.27	0.06	15.41
0.50	2.21	5.09	10.02	16.29	22.74	38.15
1.00	5.12	10.21	19.20	35.49	27.81	65.96
2.00	89.79	100.00	64.51	100.00	34.04	100.00

Table 3.2 Sieve analysis of SECC at 213 °C

| Sieve operture, mm	SECC at 213 °C for 1 min		SECC at 213 °C for 3 min		SECC at 213 °C for 5 min	
	percent of mass retained, %	Cumulative percent, %	percent of mass retained, %	Cumulative percent, %	percent of mass retained, %	Cumulative percent, %
0.00	1.01	1.01	1.23	1.23	1.02	1.02
0.08	0.02	1.03	0.53	1.76	0.44	1.46
0.11	1.15	2.18	0.75	2.51	0.79	2.25
0.15	0.28	2.46	0.75	3.26	1.14	3.39
0.18	1.49	3.95	7.54	10.80	10.07	13.46
0.36	1.20	5.15	4.13	14.93	7.65	21.11
0.42	0.17	5.32	3.28	18.21	1.17	22.28
0.50	8.69	14.01	27.28	45.49	29.51	51.79
1.00	15.51	29.52	28.69	74.18	24.68	76.47
2.00	70.48	100.00	25.82	100.00	23.53	100.00
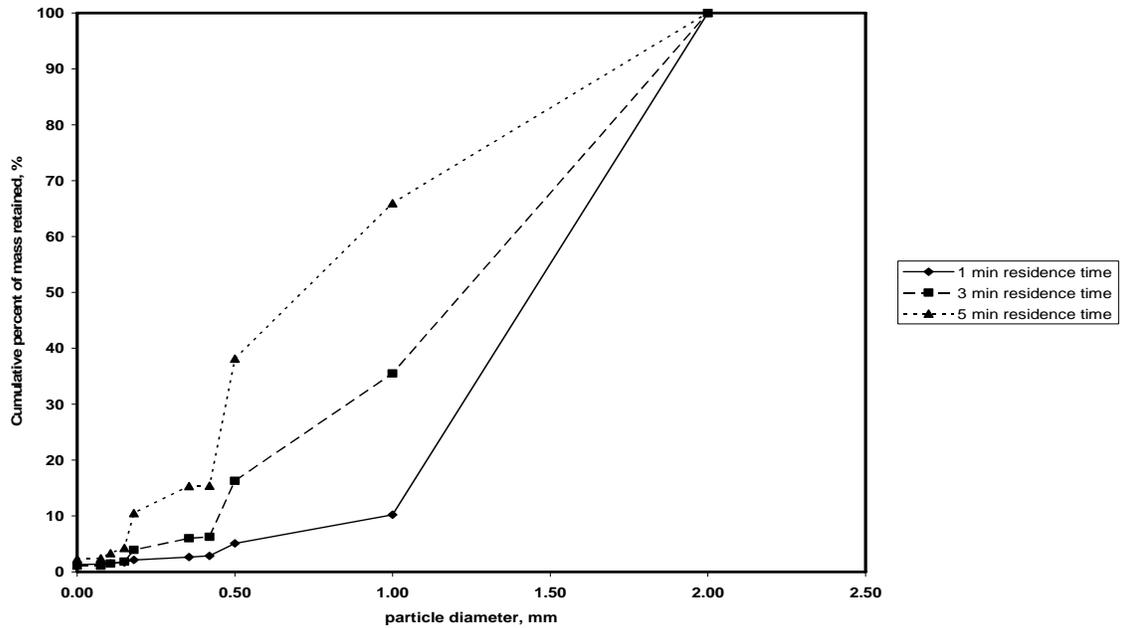
Figure 3.4 Particle size distribution of SECC at 200 ^{o}C at different reaction time
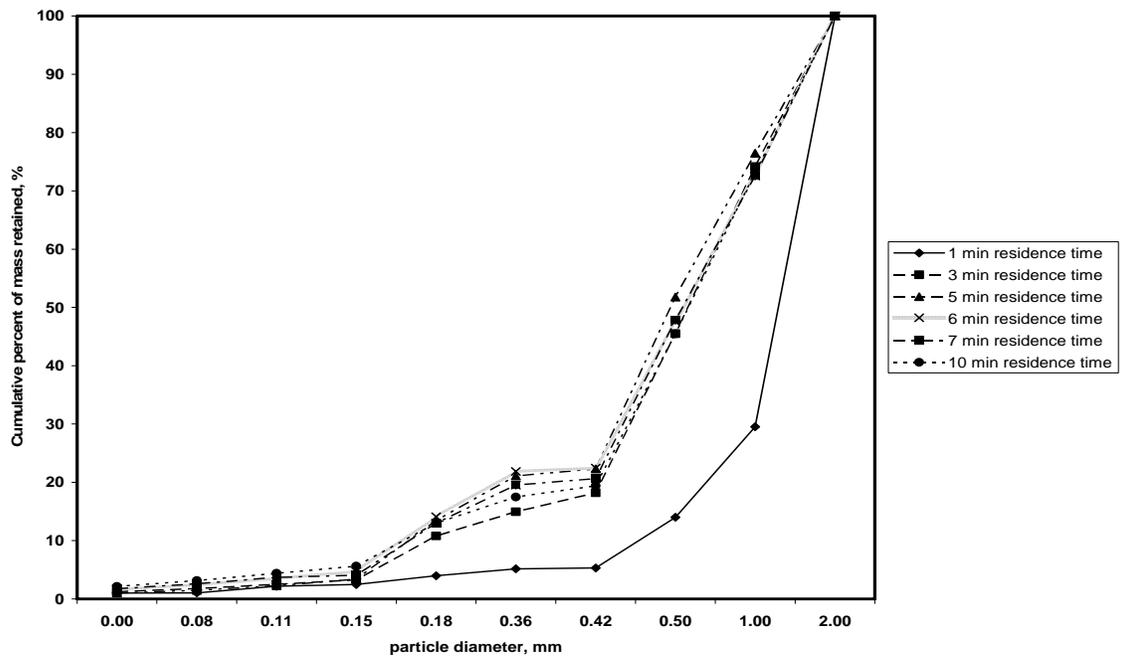

Figure 3.5 Particle size distribution of SECC at 213 ^{o}C at different reaction time

3.2.1 *Total surface Area of RCC and SECC*

The nitrogen isotherm at 77 K of raw and steam exploded corn cob are shown in Figures

3.6 and 3.7 respectively. Both isotherms are reversible type IV in the IUPAC

classification shown in Figure 2.11, section 2.8. Direct inspection of the isotherm reveals that pore filling step occurred over the relative pressures range $P/P_o = 0.35 – 0.85$ for raw corn cob (RCC) (Figure 3.4) and $P/P_o = 0.30 – 0.40$ for steam exploded corn cob (SECC) (Figure 3.5). The surprising feature of these results was the reversible pore filling step located at $P/P_o = 0.30$ for SECC. This result appears to contradict the recognized lower limit ($P/P_o = 0.42$) for hysteresis loop associated with the capillary condensation of nitrogen at 77 K (Harris, 1965). In the absence of primary micropore filling, BET analysis of the nitrogen isotherm can be used to determine the specific surface area, A_{BET}. The surface areas and the total pore volumes of various SECC are presented in Table 3.3.

Table 3.3. BET surface areas and total pore volumes of RCC and SECC samples.

Treatment temp, °C	Reaction time, min	BET, (m^2/g)	Total pore volume, (cc/g)
Untreated		3.40	1.42×10^{-2}
213	1	0.42	1.46×10^{-2}
213	5	0.59	7.86×10^{-3}
213	6	0.66	7.63×10^{-3}
213	7	0.35	4.79×10^{-3}
213	10	0.17	9.02×10^{-3}

The hysteresis loop observed in the Nitrogen isotherm for both steam exploded corn cob and raw corn cob indicates that the material is mesoporous.
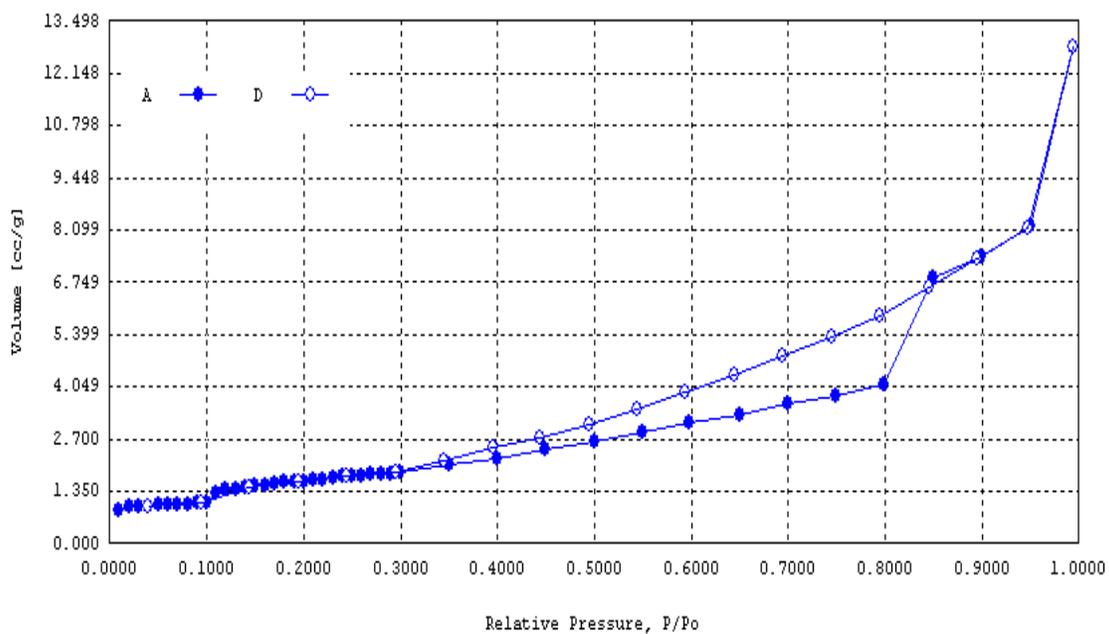
Figure 3.6 Adsorption/desorption isotherm of N_2 on RCC. A: Adsorption branch and
D: Desorption branch of the isotherm
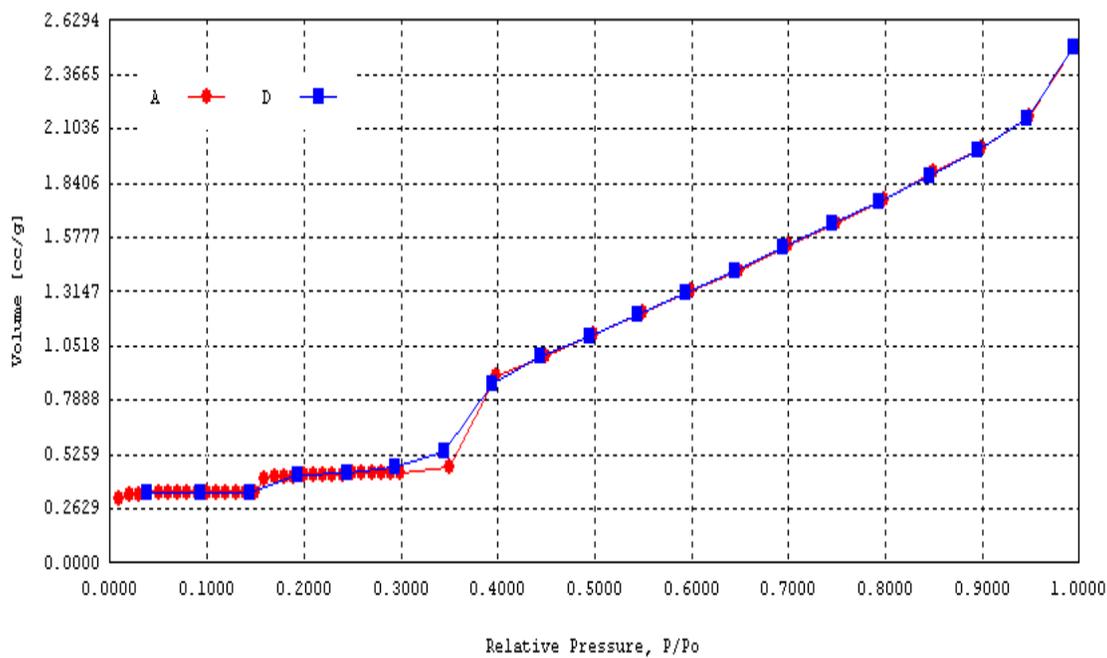
Figure 3.7. Adsorption/desorption isotherm of SECC. A: Adsorption branch and
D: Desorption branch of the isotherm

Pore volume distribution of RCC and SECC are shown in Figures 3.8 and 3.9 respectively. The pore width of RCC had a trimodal distribution consisting of 37.8 – 50 nm, 76.5nm and 270nm. The pore size of 37.8 -50nm exhibits mesoporosity while 76.5 and 270nm show macroporosity. The pore width of SECC was around 37.80 nm which indicates a mesoporous (pore width is 2 – 50 nm) material. It is interesting to note that after steam explosion the macroporous structure of the corn cob was destroyed whiles the mesoporous structure was retained; consequently, both the BET surface area and the total pore volumes decreased after steam explosion.
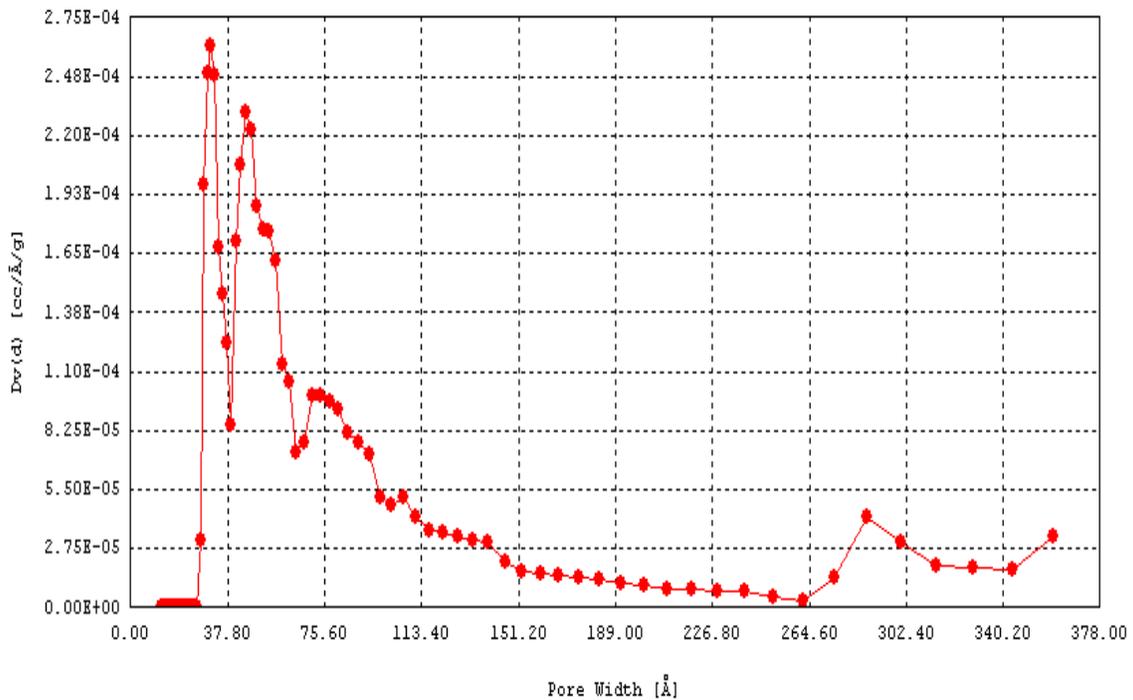
Figure 3.8 DFT/Monte-Carlo Differential Pore volume distribution of RCC
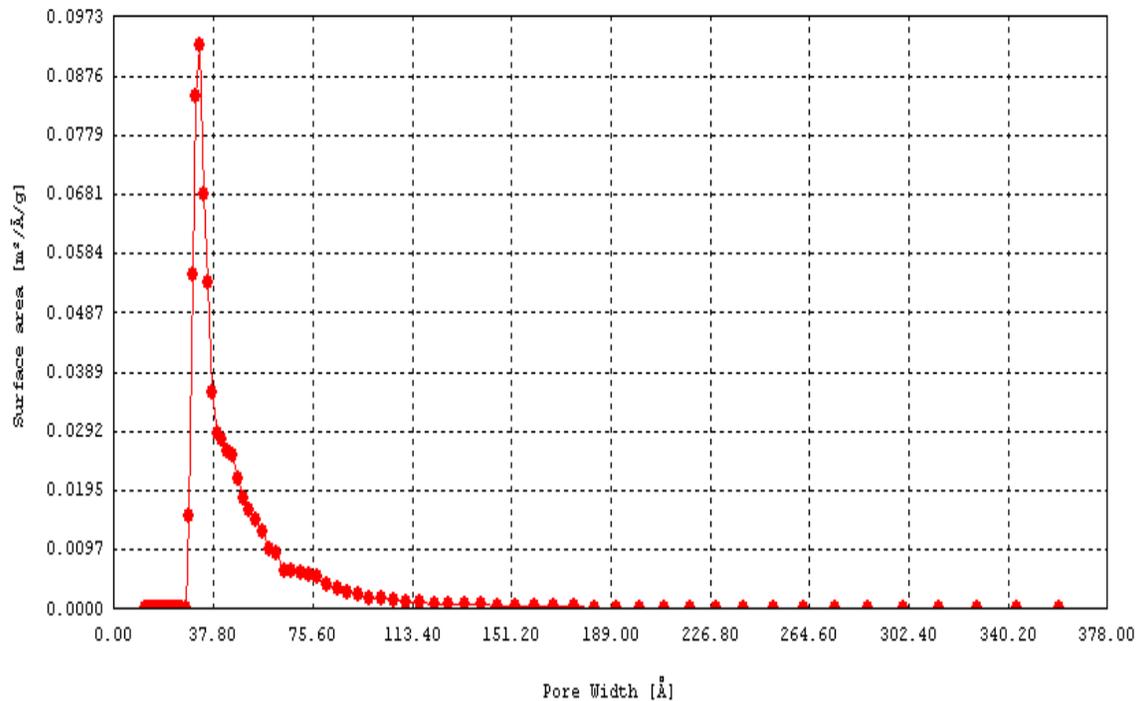
Figure 3.9 DFT/Monte-Carlo Differential Pore volume distribution of SECC

3.2.2 *Bulk Density*

Bulk density is one of the variables used in the design of adsorption columns, which affects the overall cost of the adsorption process. A high density of adsorbent does not require frequent regeneration because of its high adsorption per unit volume (U.S. Environmental Protection Agency, 1973). The bulk density results show an inverse linear relationship between the particle size and bulk density as illustrated in Figure 3.10. The average the bulk densities of RCC and SECC were 0.26 g/cm^3 and 0.47g/cm^3 respectively.
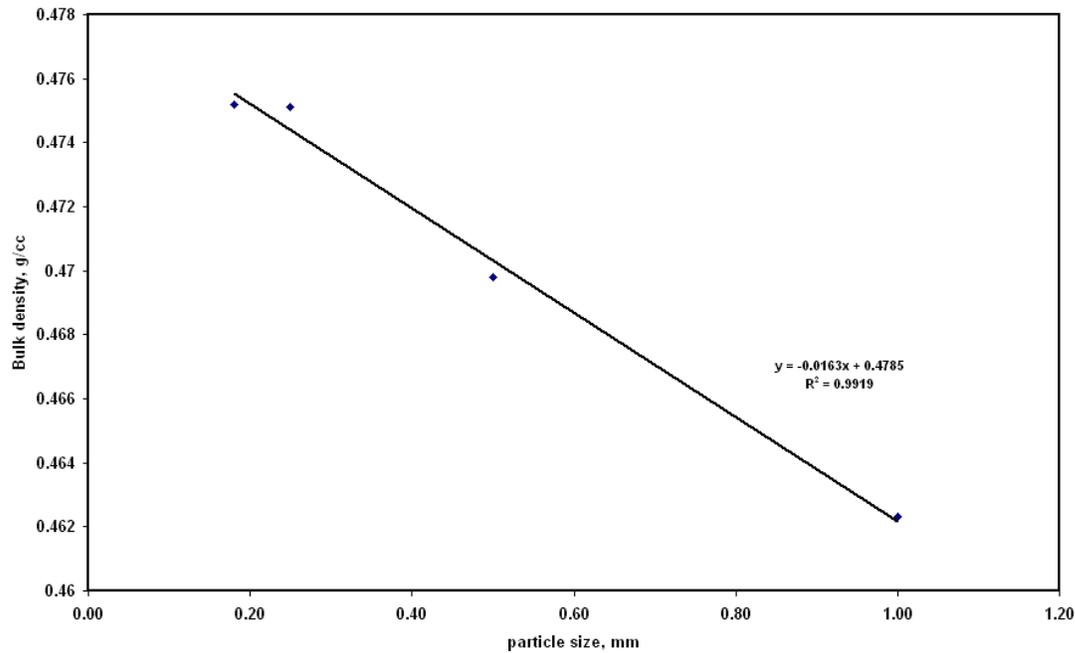
Figure 3.10 Bulk density against particle size of steam exploded corn cob

3.2.3 *Particle Density*

The particle densities of RCC and SECC were 1.12 g/cm^3 and 1.43 g/cm^3 respectively. Since the design of a packed column or fixed bed reactor has a fixed volume, for a given weight capacity, the adsorbent with a higher density will give a higher volume capacity (Luping, 2000). Thus, since the SECC has is denser than the RCC, we expect the SECC to have a higher volume capacity and therefore more suitable than the raw corn cob.

3.2.4 *Ash Content*

Ash content is the measure of the minerals such as Ca, Na, K and Cl present as impurities in the material. The ash content of RCC decreased from 3.43% to 1.94% after steam explosion. The reduction in the ash content of SECC may be due to the dissolution of potassium and other minerals in the water during the steam treatment of RCC.

3.2.5 Adsorption Experiments.

3.2.5.1 Batch studies

The amounts of NH_4OH consumed by both the raw and steam exploded are presented in Table 3.4. In all cases both raw and steam exploded corn cob removed ammonia. The amount of NH_4OH that reacted with the RCC was fourteen times that of the SECC. (Table 3.4 and Fig 3.12). The pretreatment impacted some acidic properties thereby making the whole interaction as that of acid base. The ammonia removal capacity of the steam exploded corn cob was further enhanced when augmented with acidic salts of aluminum sulfate hydrate, $Al_2(SO_4)_3.xH_2O$ and iron sulfate hydrate, $Fe_2(SO_4)_3.xH_2O$. The NH_4OH consumed increased linearly with increase in salt content. This is evident in Figure 3.11 which shows the correlation coefficient (R^2) of both salts greater than 0.95.

Table 3.4 Amount of NH_4OH reacted with both RCC, SECC and salts addition

Sample	Adsorption capacity, mgNH$_4$OH/gSample	
RCC	0.0328	
SECC	0.4725	
Salts : SECC	$Al_2(SO_4)_2.xH_2O$	$Fe_2(SO_4)_3.xH_2O$
1:99	0.6650	0.5950
2:98	0.8225	0.7700
3:97	0.9975	1.1200
5:95	1.1375	1.3125
9:91	2.0475	2.4350

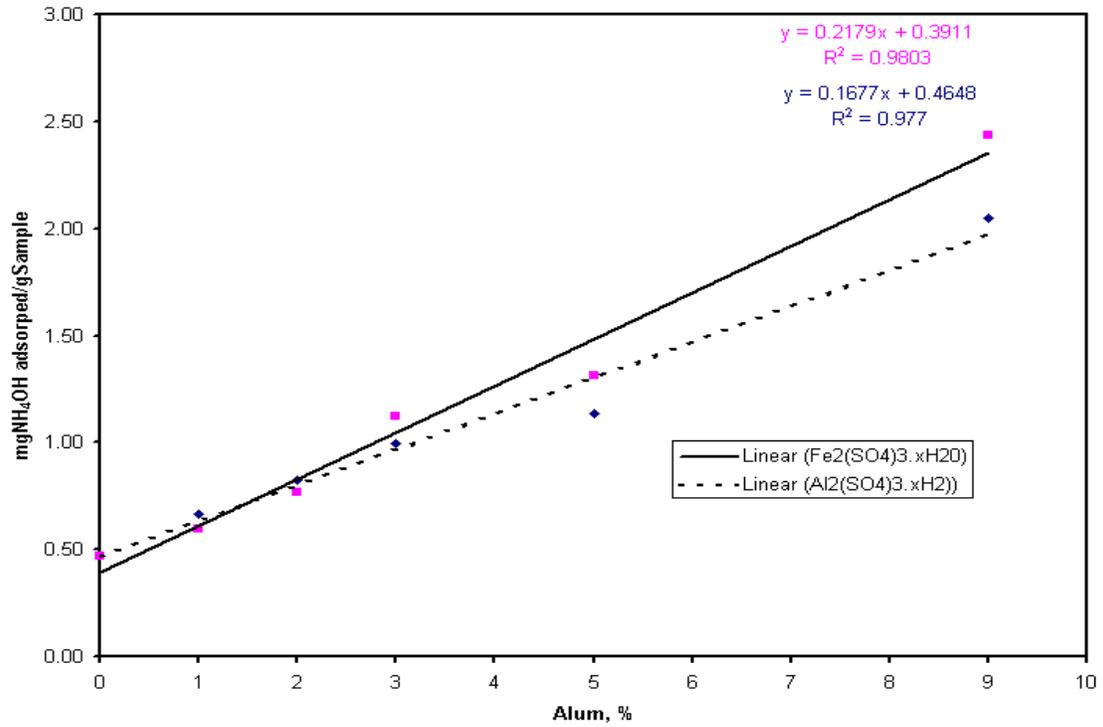Note: RCC = Raw corn cob and SECC = Steam exploded corn cob

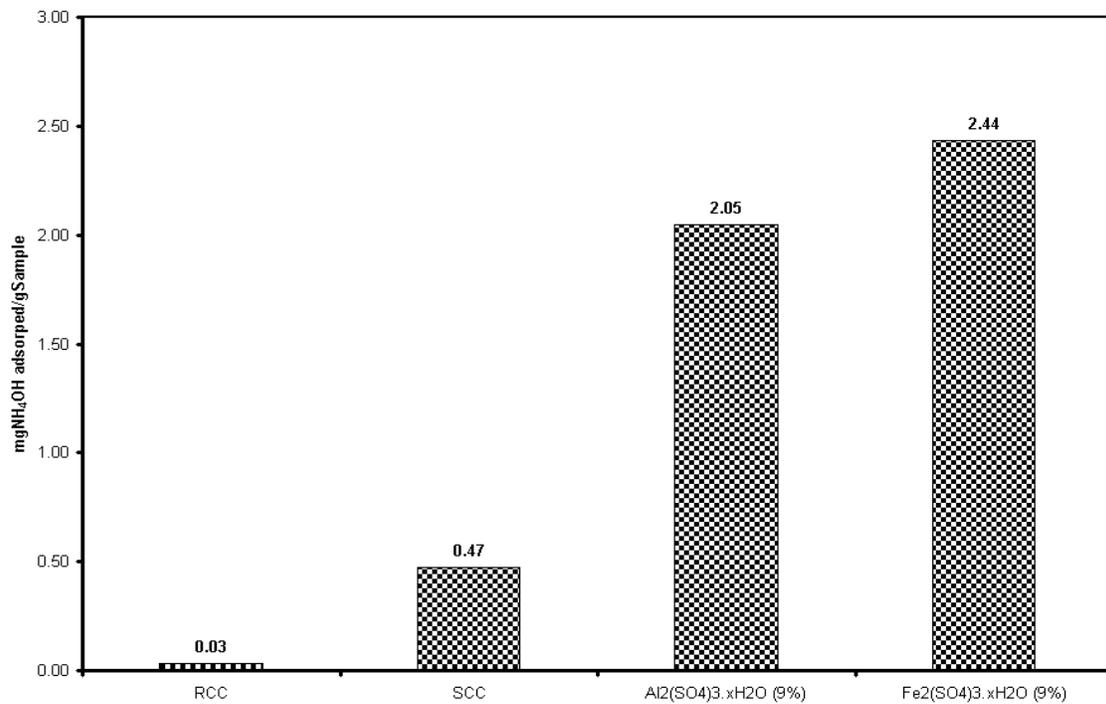Figure 3.11 Adsorption capacity of SECC with Alum against 0.05 M NH$_4$OH

Figure 3.12 Adsorption capacities of samples with 0.05M NH$_4$OH

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3.2.5.2 Column studies

The dynamic studies using the custom made packed bed reactor revealed that ammonia was effectively removed by this system (Table 3.5). The reaction was exothermic generating more than 2 ^{o}C per gram of SECC material (Figures 3.13, 3.14 and 3.15). The maximum adsorption capacity of 59.8 mgNH$_3$ per gSECC was achieved when the raw corn cob was steam exploded at severity factor of 3.84 and the lowest adsorption capacity of 37.00 mg NH$_3$ per gSECC was recorded at severity of 2.94. The high uptake of ammonia could be attributed to acidic compounds released during the steam treatment. The acidity of the SECC appeared to be strongly influenced by the severity of the steam explosion if the temperature is kept constant and the time of treatment was increased (Table 3.4). The only anomaly was the severity of 4.33 which did not experience any decrease in pH as expected (see Figure 3.16). The reaction temperature also appeared to have a strong influence on the pH of the SECC. Although the severity factor for reaction at 220 ^{o}C and 2 min (3.83) was lower than that at 213 ^{o}C and 10 min (4.33), the adsorption capacity the SECC was higher (Figure 3.17). Thus it appears in this case the temperature based severity factor has a stronger influence than that due to the time based severity factor which is in agreement with Jeoh and Agblevor (2001). The interaction of ammonia with the steam exploded corn cob appears to be strongly influenced by acid-base reaction. Although the surface area of the RCC was greater than the SECC, its adsorption capacity appears to be lower than that of the SECC. Thus the pH of the adsorbent appears to have a strong influence on the ammonia (Figure 3.18).

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Table 3.5 Adsorption capacity and pH of SECC at different severities

Sample #	Temperature, oC	Residence time, min	Severity factor	pH	Adsorption capacity, mg/gSample
1	0	0	0.00	4.86	10.45
2	200	1	2.94	4.60	37.00
3	200	3	3.42	4.09	41.58
4	200	5	3.64	4.04	45.00
5	213	1	3.33	4.30	47.58
6	213	3	3.80	3.97	56.35
7	213	5	4.03	3.87	56.37
8	213	6	4.11	3.74	56.87
9	213	7	4.17	3.72	58.97
10	213	10	4.33	4.07	49.50
11	220	2	3.83	3.78	59.80

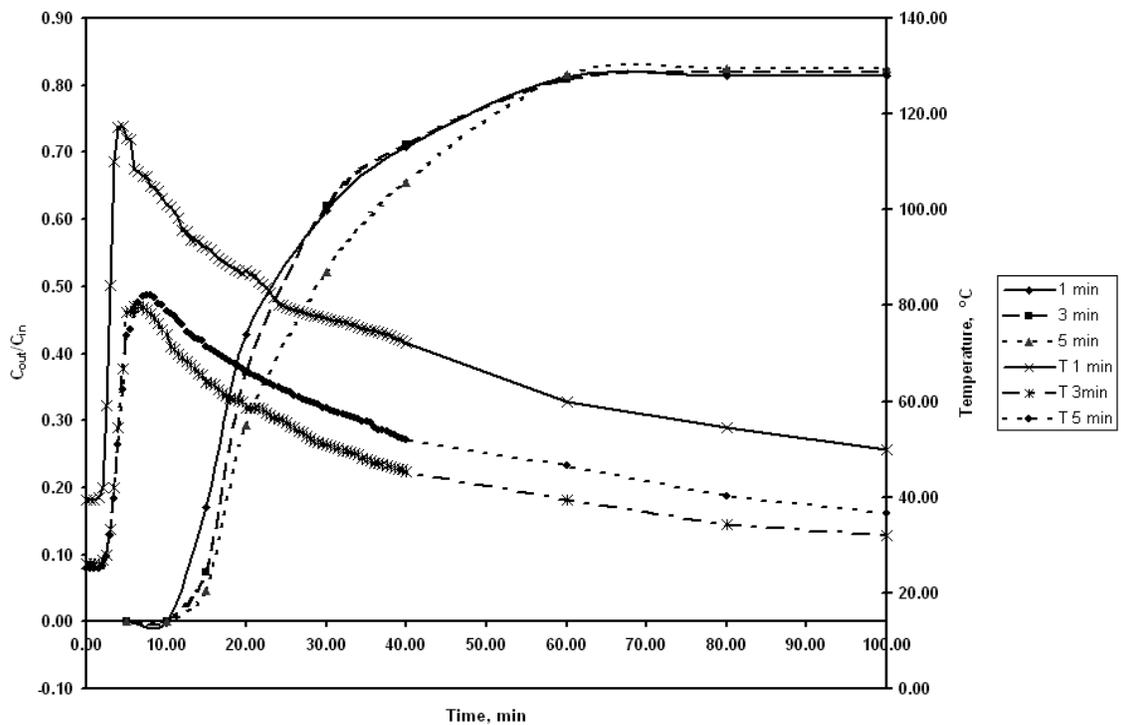Figure 3.13 Breakthrough curve of ammonia adsorption of SECC at 200 $^{\circ}$C
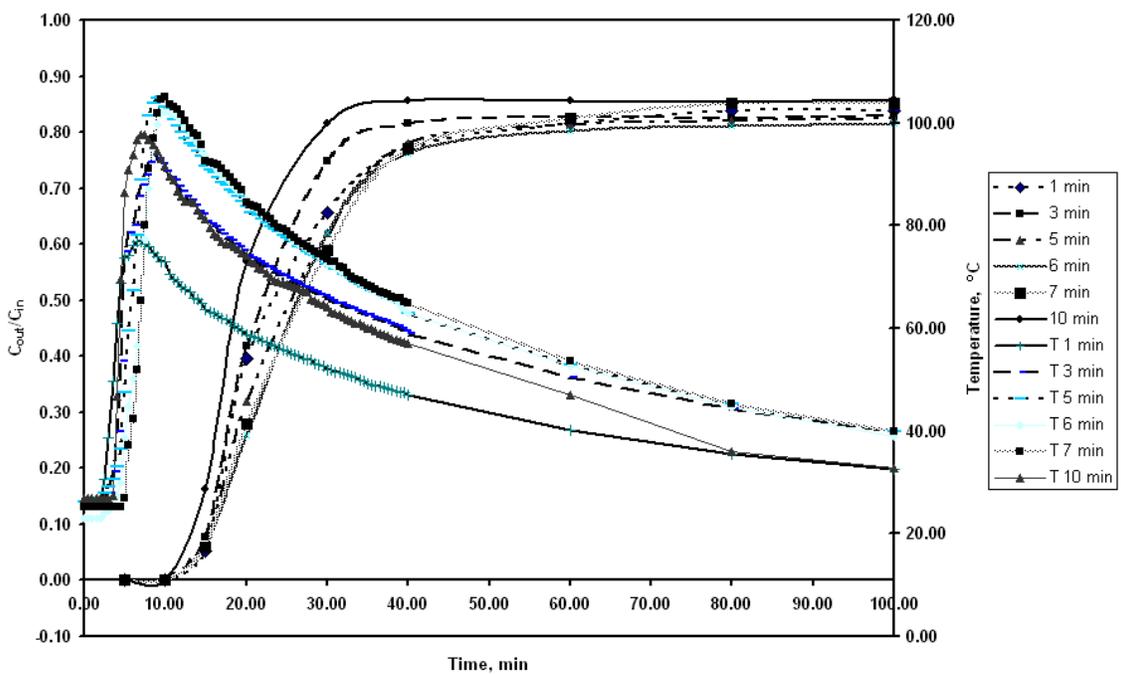
Figure 3.14 Breakthrough curve of ammonia adsorption of SECC at 213 $^{\circ}$C
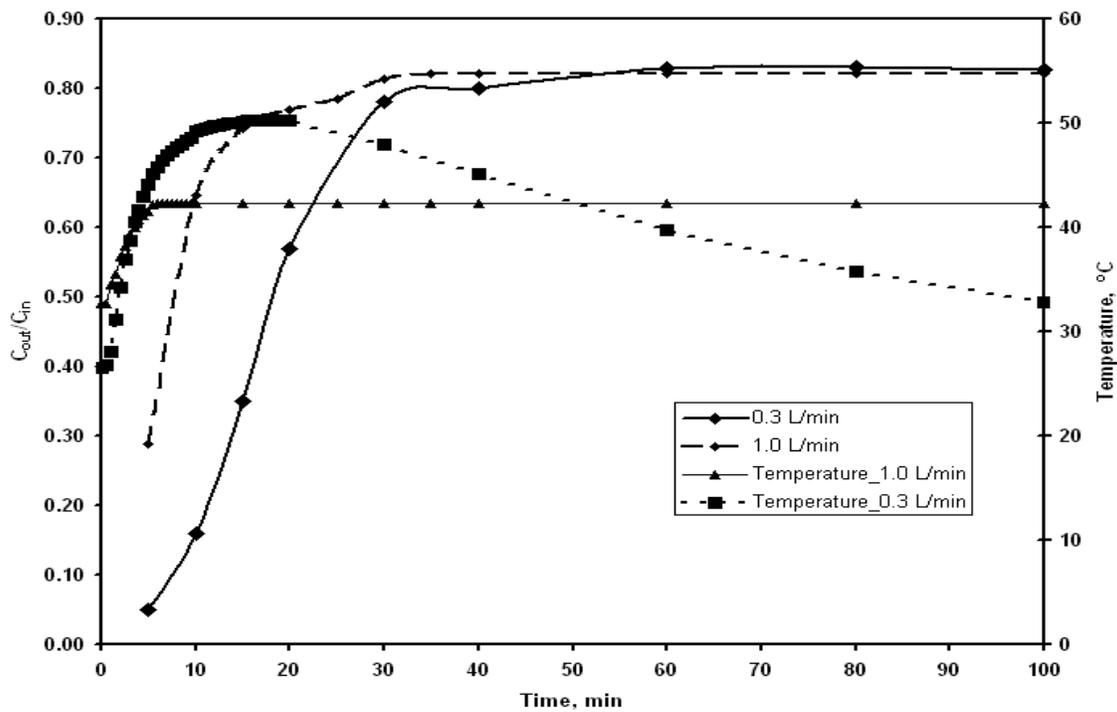
Figure 3.15 Breakthrough curve of ammonia adsorption of SCC at 220 ^{o}C
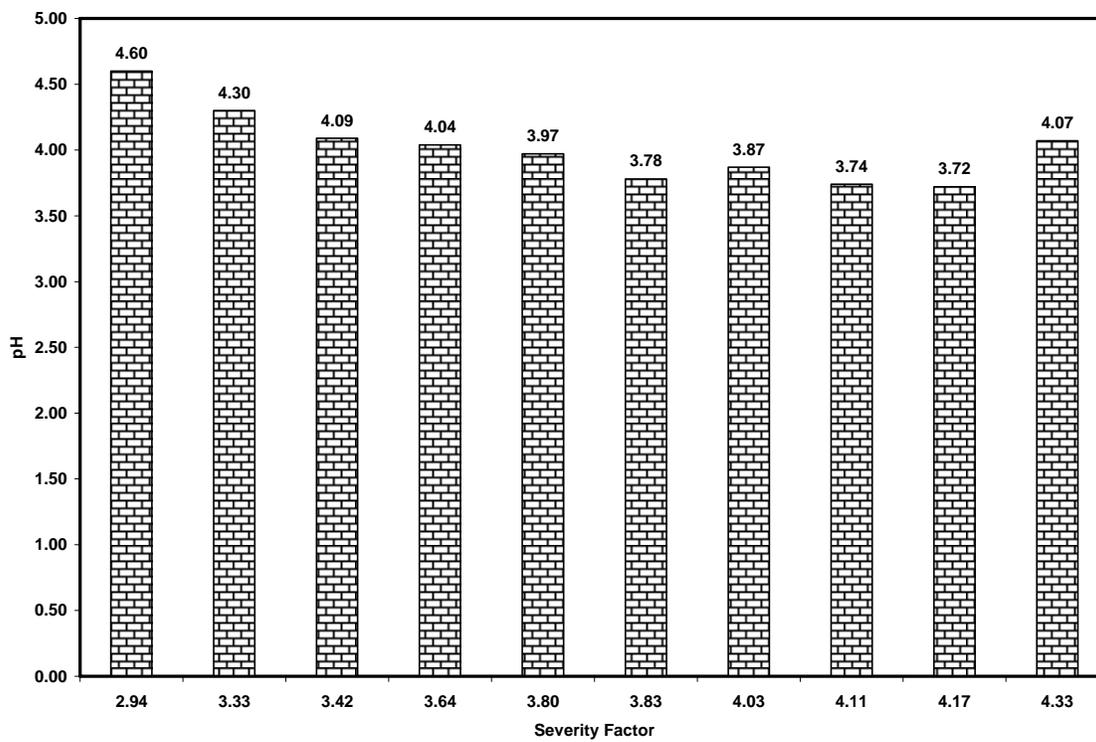
Figure 3.16 Effect of severity factor on the pH of SECC
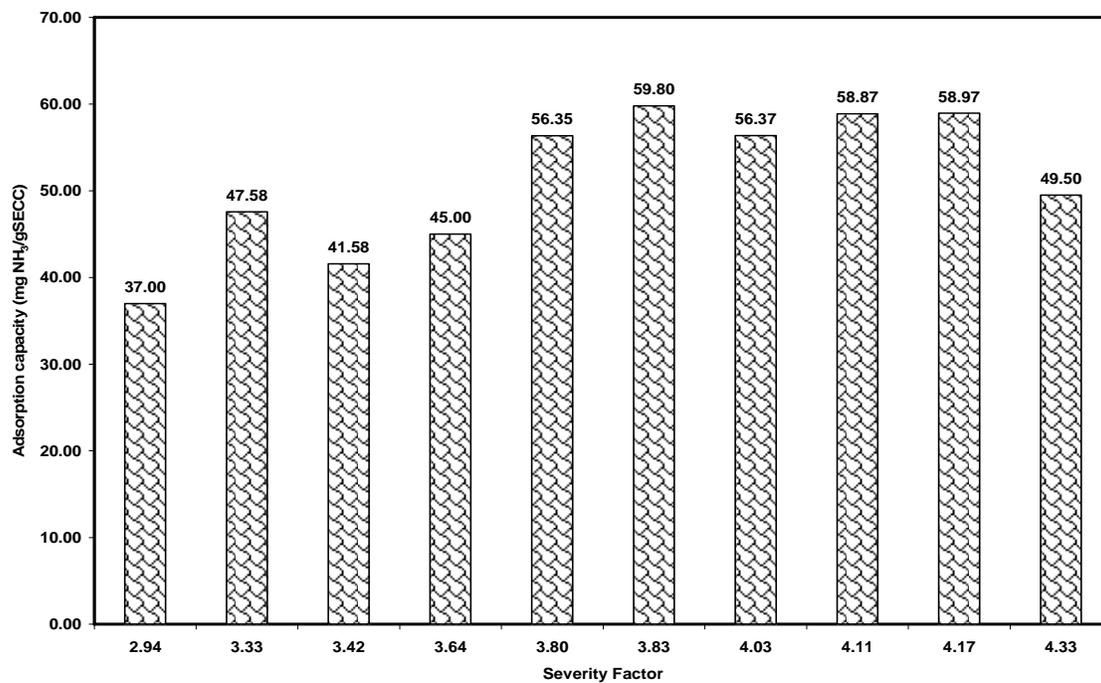
Figure 3.17 The effect of severity factor on adsorption capacity of SECC
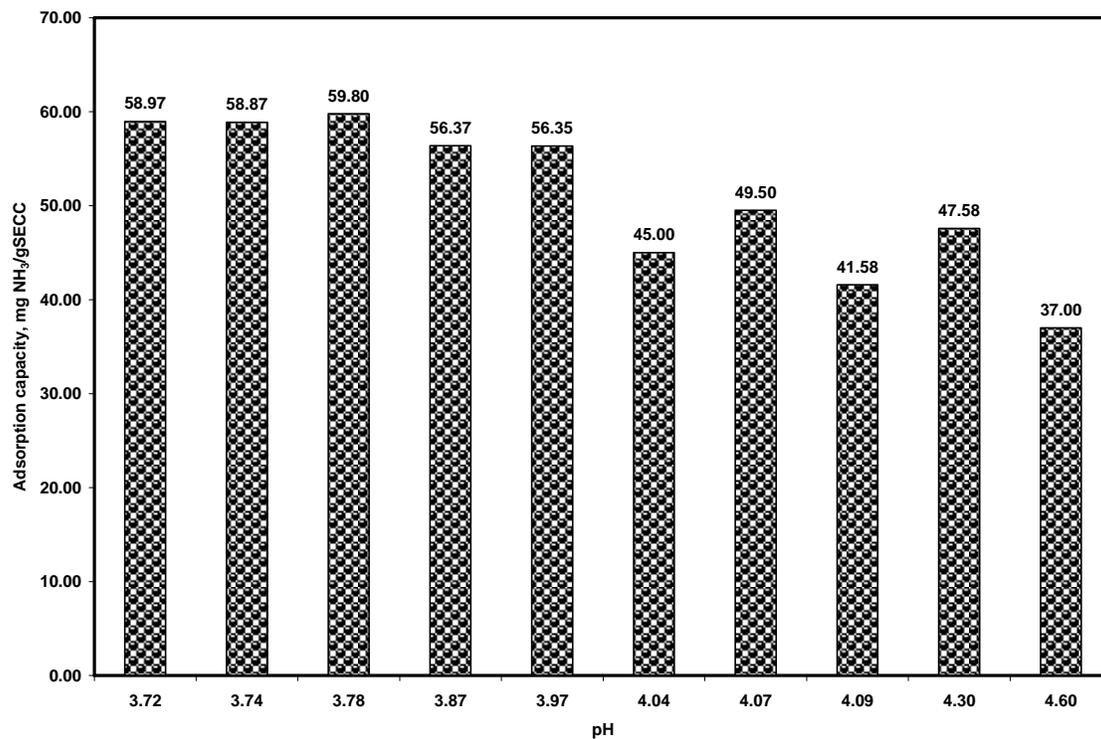
Figure 3.18 The effect pH on adsorption capacity of SECC

When SECC was impregnated with the acidic salts, the ammonia removal capacity of SECC improved slightly (Tables 3.6 and 3.7). Addition of 1% $Al_2(SO_4)_3.xH_2O$ and $Fe_2(SO_4)_3.xH_2O$ to SECC increased the adsorption capacity by 1.00 and 1.02 times respectively. When 9% of both salts was added to SECC, the adsorption capacity of $Al_2(SO_4)_3.xH_2O$ increased by 1.10 whilst that of $Fe_2(SO_4)_3.xH_2O$ increased by a factor of 1.41. Although the improvement of the SECC was not dramatic as expected it showed signs of enhancing SECC. The adsorption capacity of the impregnated SECC was dependent on the pH since lower pH favors higher uptake of ammonia (Figure 3.19). However, a nonlinear relationship was observed between pH of the adsorbent and percent of alum added. The impregnated SECC became more acidic as higher percentages of both salts were added (Figure 3.20)

Table 3.6 Adsorption capacity of impregnated SECC with $Al_2(SO_4)_3.xH_2O$

Sample #	Temperature, oC	Residence time, min	Severity factor	pH	Adsorption capacity, mg/gSECC
$Al_2(SO_4)_3.xH_2O$:SECC					
SECC	213	7	4.17	3.72	58.97
1:99	213	7	4.17	3.59	59.00
3:97	213	7	4.17	3.38	59.40
5:95	213	7	4.17	3.36	60.00
9:91	213	7	4.17	2.99	65.00
$Al_2(SO_4)_3.xH_2O$	0	0	0.00	3.69	**175.54**

Table 3.7 Adsorption capacity of impregnated SECC with $Fe_2(SO_4)_3.xH_2O$

Sample #	Temperature, ^oC	Residence time, min	Severity factor	pH	Adsorption capacity, mg/gSECC
$Fe_2(SO_4)_3.xH_2O$:SECC					
SECC	213	7	4.17	3.72	58.97
1:99	213	7	4.17	3.33	59.00
3:97	213	7	4.17	2.97	59.40
5:95	213	7	4.17	2.81	60.00
9:91	213	7	4.17	2.59	65.00
$Fe_2(SO_4)_3.xH_2O$	0	0	0.00	2.10	180.62
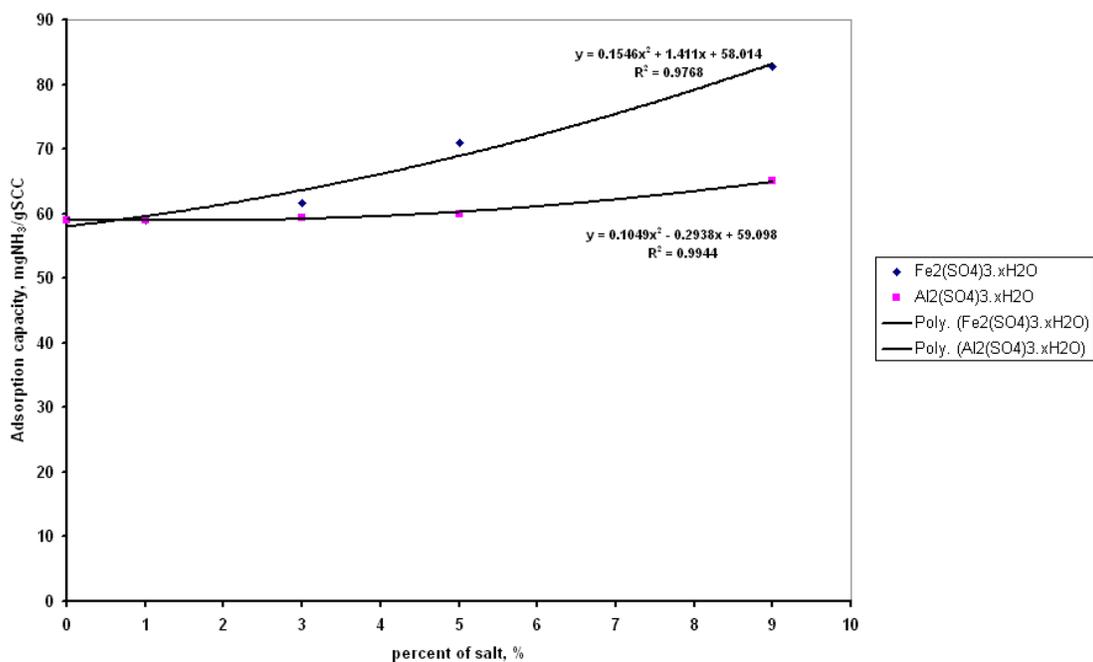
Figure 3.19 Ammonia adsorption capacity of Impregnated Steam exploded corn cob
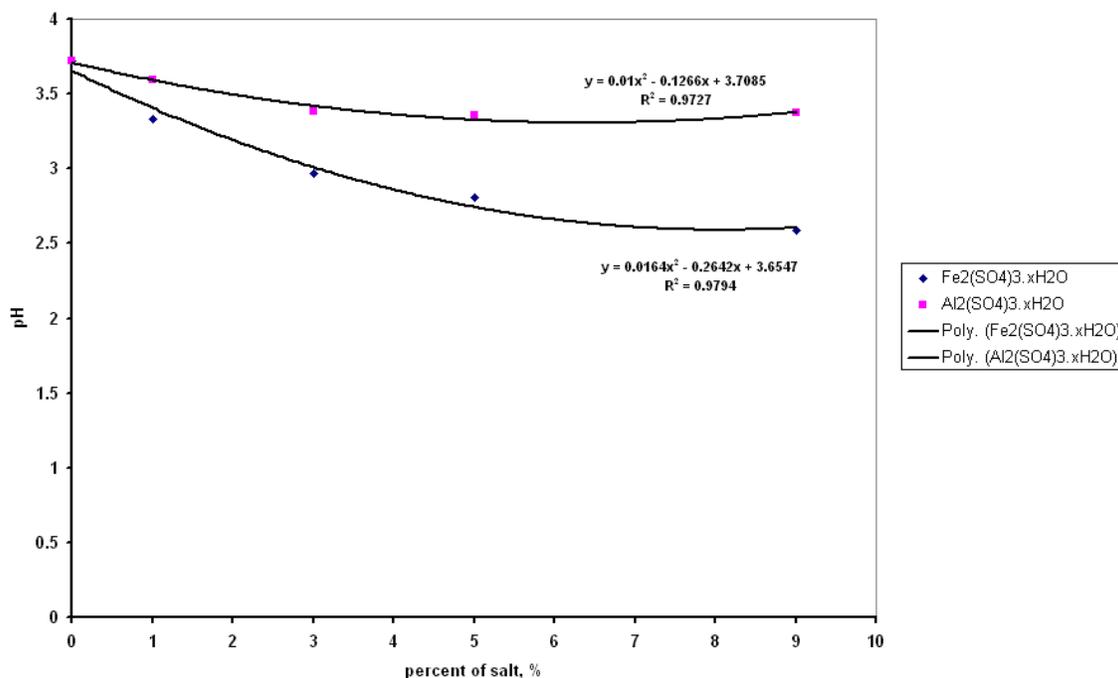
Figure 3.20 pH of Impregnated Steam exploded corn cob

3.2.5.3 Comparison of Ammonia Removal by Titration and Packed Column

The data clearly showed that ammonia removal using the titration method is several times larger than that achieved using the packed column. In the case of the titration method, the SECC was suspended in water and then titrated with NH_4OH. The ratio of NH_4OH removed by the SECC compared to the raw corn cob was 14.4 times. However, when the two materials were packed in the column and NH_3 as was passed over them, the ratio of NH_3 removed per gram of the SECC compared to the raw corn cob was 5.7 times. This apparent contradictory results can be attributed to the following:

1) In the case of the titration, since the SECC contain organic acids on both its surface and in the pores, the water addition prior to the titration caused the organic acids to diffuse into the water and these were readily titrated resulting in large amounts of NH_4OH consumed per gram of SECC, and

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2) In case of the packed column, the removal of NH_3 will be influenced by several factors including: (a) surface area of the particles, (b) pore size of particles, (c) diffusivity of ammonia through the pores, (d) equilibration of ammonia in the packed bed, (e) ammonia gas flow rate and blockage of pores by NH_3 reaction products.

If SECC pore sizes are small, then at high NH_3 gas flow rates, most of the reaction will only take place on the exterior surface of the particles with very little diffusion into the interior of the particles. For very low flow rates, the chances of diffusion into the interior of the particles increase. Thus, it appears that in the case of the column experiment, there was diffusion limitation and ammonia reaction took place only on the surface of the particles. Since the interior surface area of pores are normally larger than the external surface area for porous materials, it appears a large fraction of the material in the packed column did not react with the ammonia. It is also plausible that some of the reaction products of the NH_3 with SECC could have blocked some of the pores and thus reducing the probability of NH_3 diffusing into the pores and reacting with it.

3.2.5.4 Comparison of Impregnation of SECC with acid salts versus simple additive mixtures

The simple addition of acidic salts of aluminum sulfate hydrate, $Al_2(SO_4)_3.xH_2O$ and iron sulfate hydrate, $Fe_2(SO_4)_3.xH_2O$ to SECC before titration with NH_4OH showed a direct linear correlation between the amount of acid added and the amount of NH_4OH consumed. Even small amounts of salt (1%) appeared to have enhanced the NH_4OH removal. However, for the impregnated SECC, the salts had no effect on the ammonia removal until the percentage of salt was raised to 9%. For the case of simple salt addition,

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at 9%, improvement was 4.3 times for $Al_2(SO_4)_3.xH_2O$ and 5.15 times for the $Fe_2(SO_4)_3.xH_2O$ (See Table 3.3). However, for the impregnated SECC; the improvements at 9% addition were 2.98 times for $Al_2(SO_4)_3.xH_2O$ and 3.06 times for $Fe_2(SO_4)_3.xH_2O$ (See Table 3.5). The differences in the improvements in the ammonia removal could also be attributed to the gas flow rate and diffusion effect.

3.3 Conclusions

The present results show that a novel biodegradable adsorbents based on steam explosion technology has been developed and tested. The acidity of the steam exploded corn cob is a factor for the high uptake of ammonia on the steam exploded corn cob. The more acidic the steam exploded corn cob the higher the ammonia adsorption capacity.

It is obvious from these results that the steam exploded corn cob impregnated with aluminum sulfate hydrate, $Al_2(SO_4)_3.xH_2O$ and iron sulfate hydrate, $Fe_2(SO_4)_3.xH_2O$ are good candidates for the practical applications in removing ammonia. This increase is caused by the chemical reaction of ammonia with acid remaining in the pores of steam exploded corn cob. The results also reveal interesting information that an increase in the salts impregnation level, e.g., from 5 to 9%, did not improve the adsorption capacity significantly in the case column studies. The possible explanation to this may be due diffusion limitation.

The apparent contradictory results from the titration and packed column may be due to ammonia gas flow rate and subsequent diffusion limitation due to short residence time of the gas in the packed bed. This study shows that SECC could be potentially used to remove NH_3 from various emission sources

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CHAPTER FOUR

INSTRUMENTAL CHARACTERIZATION OF STEAM EXPLODED CORN COB

ABSTRACT

The adsorption of ammonia on steam exploded corn cob, SECC was studied with a custom made packed column reactor, Attenuated Total Reflection Fourier Transform Infrared, (ATR-FTIR) spectroscopy in the range 4000–700 cm^{-1}, and Simultaneous DSC - TGA Analyzer. The packed column studies showed that the maximum adsorption capacities of the raw corn cob (RCC) and the steam exploded corn cob (SECC) were respectively 10.45 mg NH_3/g RCC and 59.80 mg NH_3/g SECC. The FTIR bands in the region between 1500 and 2000 cm^{-1} showed a considerable difference between RCC and SECC. When SECC was treated with ammonia, the carboxylic functional group peak at 1700cm^{-1} was reduced and a new peak was observed at 1584cm^{-1}. The adsorption, desorption test and the heat of adsorption results suggested combined physisorption and chemisorption of ammonia on SECC but chemisorption was found to play an important role in ammonia removal. The heat of adsorption of ammonia on SECC was determined by integrating the peak area of the DSC signal and was 33.00 kJ per mole of ammonia.

Keywords: Corn cob, Adsorption, Steam explosion, Chemisorption, Physisorption

4.0 Introduction

Ammonia is a colorless, irritant, and corrosive gas produced by decomposition of organic materials, and fertilizer production and utilization (Arogo et al., 2006). The gas can be detected by most people at a concentration of 50ppm in the air. Breathing levels of 50-100 ppm NH_3 can give rise to eye, throat, and nose irritation (Heber et al., 2002). Most abatement methods adopted to reduce ammonia can be categorized into two types namely: the destructive methods (thermal oxidation and catalytic oxidation) and the recuperative methods (adsorption, absorption, condensation and separation by membranes) which allows for the recovery of the gas. Among these methods, adsorption has gained prominence for its being very effective in dealing with low pollutant concentration levels, and for making it possible for the recovery of the pollutant through desorption (Heumann, 1997). In this process, an adsorbent with high surface area and chemical surface functionalities is used. Activated carbon is the most successful and widely used due to its safety and effectiveness in operation process (Cheremisinoff et al., 1993).

In recent times, there has been a large impetus given to the development of low cost activated carbon for the treatment of air pollutants. Most of these activated carbon are usually developed from agricultural residue such as wheat (Lanzetta et al., 1997), corn hulls (Zhang et al., 2004), hazelnut shells (Aygun et al., 2003), pecan shells (Cetin et al., 2004) and rice husks (Malik et al.; 2003 & Yalcın and Sevinc, 2000). The process economics of preparing these is heavily dependent upon the processing method adopted. The widely used adsorbent, activated carbon is normally produced using a two way process namely carbonization and activation at elated temperatures. Since the technology

of waste gas treatment is often dictated by economy and ecological constraints, there is the need to develop newer products, bearing in mind the overall cost and whether the technology is benign to the environment. Steam explosion has gained a lot of popularity as being a novel pretreatment method for biomass fractionation. Steam pretreatment involves heating biomass at high temperatures and pressures, followed by mechanical disruption of the pretreated material (Ramos et al., 1994). The high-pressure steam modifies the plant cell wall structure, yielding a dark brown material. The pretreatment process can be carried out with or without addition of an acid catalyst (Ramos et al., 1992). When no acid is added to the biomass the process is termed autohydrolysis and acetic acid which is released from acetylated hemicelluloses is considered the main catalyst of the autohydrolysis (Ramos, 2003). Apart of acetic acids produced during the process, other acids like formic and levulinic acids are also produced and may also impact the pretreatment process efficiency (Ramos, 2003). This pretreatment method influences both surface and acidic properties to the fractionated material.

To date, no record is found in the literature that utilizes the steam explosion method to produce adsorbent. In this study, a new adsorbent was produced from corn cob using the steam explosion technology. Structurally, a corn cob is composed of four constituent parts: (1) the outer glume, (2) the beeswing, (3) the woody ring, and (4) the pith. In comparison, the outer glume, beeswing and pith portions of the cob are much lighter in weight and much more absorbent than the woody ring portion of the cob. Corncobs are often considered as waste material from industrial utilization of maize crops. There are several applications of corncobs reported in the literature. For example, pulverized corncobs were used to produce lignocellulosic composites (Rowell et al., 1997);

polypropylene and other engineering polymers have been reinforced with pulverized corncob fiber (Youngquist and Krzysik, 1993). Corncobs, being largely cellulose and hemicelluloses, possess excellent absorption properties and are used in a variety of applications as chemical spill absorbents, animal bedding, and as a carrier of agricultural fertilizers (McPherson et al., 1968). Corncobs have also been transformed to activated carbon and used as a sorbent (Tsai et al., 2001). The goal of this study was to accomplish the following objectives:

1. investigate the various type of functional groups in raw and steam exploded corn cob

2. utilize dynamic adsorption method to determine the ammonia adsorption capacity of steam exploded corn cob

3. examine whether the adsorption process led to the formation of a chemical bond (chemisorption) or the phenomenon is governed by physical interaction between the adsorbate (ammonia) and the adsorbent (steam exploded corn cob)

Identifying functional groups on the surface of adsorbent is not an easy task. The methods normally used in determination of weakly acidic groups are direct titration, IR spectroscopic analysis and X-ray photoelectron spectroscopy. IR spectroscopy provides information on functional groups within the material. The Fourier-transformed infrared (FTIR) spectroscopy, is a measurement technique in which spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

The properties of most adsorbents are dependent on the textual characteristics and the chemical functionalities. The former are described by the surface area and porosity, and

the latter mainly by the chemical groups on the surface of the adsorbent. These functional groups show whether the adsorbent is acidic, basic or neutral. Mapes and Eischens (1954) demonstrated the power and utility of IR studies of chemisorbed ammonia and provided direct experimental evidence for the existence of Lewis and Brønsted acidity on the surfaces of activated carbon. Apart from IR spectroscopic analysis, X-ray photoelectron spectroscopy is used to study the functional group of materials. X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. Clave et al., 2003, demonstrated the use of X-ray photoelectron spectroscopy to study the surface chemistry of corn cob. Their results showed that the carbon peak consists of four component peaks: C_1, C_2, C_3, and C_4 at approximately 284.6, 286.2, 287.6, and 289 eV, respectively. The C_1 component of corn cob was assigned to carbon atoms bound to carbon or hydrogen (C-C and/or C=C and/or C-H), which could be due to the lignin component in corn cob. C_2 was ascribed to carbon singly bonded to a single oxygen (C-OR and/or C-OH) which could originate from both carbohydrates and lignin. Finally, C_3 was assigned to carbon singly bonded to two oxygen atoms or double-bonded to a single oxygen (O-C-O and/or C=O) and C_4 was assigned to carbon of carboxylic acids and esters (O-C=O). The C_3 and C_4 component were assigned to acetyl linkage and reducing end groups of carbohydrates, with a small contribution possibly from carbonyl groups of lignin and the carboxylic acid or acetyl groups of hemicelluloses respectively.

Most gas adsorption on a solid surface is a spontaneous, exothermic process and is normally accompanied by a decrease in the free energy of the system. The highest heat of adsorption, could be hundreds of kJ/mol adsorbate, is the characteristic of chemisorption. During physical adsorption, ammonia is bound to the material by so-called adsorptions and released heat which is in the order of dozens kJ/mol of adsorbate. The magnitude of activation energy gives an idea about the type of adsorption. The physisorption processes usually have energies in the range of 5-40kJ/mol while higher activation energies 40-800kJ/mol suggests chemisorption (Nollet et al, 2003). According to Kijenski and Baiker (1989), the two best methods for investigating the strength of acid sites is the calorimetric measurement of the heat of adsorption of the based molecule and temperature programmed desorption (TPD). These techniques normally provide basic information on the type of reaction governing the adsorbate-adsorbent interaction, especially when the interaction leads to chemisorption. Calorimetric measurements provide a quantitative thermodynamic scale of acidity by allowing a direct measure of the heat of adsorption of a molecule. The differential scanning calorimetry referred to as DSC is an established calorimetric analytical method currently used for heat of adsorption measurement. To fully understand the adsorption mechanism, the DSC method was employed. Apart from determining the surface functionalities of the adsorbent it is important to investigate the heat of adsorption of the adsorbate.

4.1 Experimental Section

4.1.1 Materials

Anhydrous ammonia (99.5%) (Airgas Inc, VA USA) was used as a model gas for this study. An amount of 40g/liter of Boric acid (Fisher Scientific Inc., Pittsburgh, PA) was used to absorbed ammonia during the column studies. A 1.0M of Hydrochloric acid, HCl (Fisher Scientific Inc., Pittsburgh, PA) was prepared and used as the titrant.

4.1.2 Apparatus

The experimental apparatus was a custom made fixed design with temperature measuring thermocouples. Schematic diagram of the experimental set up is shown in Figure 3.1 and the various apparatus used are the same as those used in section 3.1.1.

4.1.3 Preparation of steam exploded corn cob material

The steam exploded corn cob was prepared in a 25-liter batch reactor located at the Thomas M. Brooks Forest Products Center (Virginia Tech). See section 3.1.2.1 for detailed method used for preparation of SECC material.

4.1.4 Dynamic Ammonia adsorption Procedure

Dynamic tests were carried out at room temperature to evaluate the capacity of the steam exploded corn cob for NH_3 removal. Adsorbents samples were sieved and (0.5–1.0 mm particle size) used for the adsorption experiment. Titration was used to determine the mass of ammonia adsorbed by the steam exploded corn cob. The ammonia gas was bubbled through a 400 ml cold boric acid solution for 5 min and then titrated with 40g/l of boric acid. The difference between the titrant and the initial concentration of boric acid was determined as the ammonia consumed. The adsorption column used in the experiments was 60mm in diameter and 600mm in height. It was made of glass and

insulated to minimize effects related to heat loss. An adsorbent sample of mass of 50.0g was used. Prior to feeding the reactor with ammonia gas, the total reactor and its content were weighed. After the bed reaching saturation, the experiment was stopped and the reactor and its content were weighed again. Afterwards, a new set of experiments was started with the other samples. The experimental setup is shown in Figure 4.0
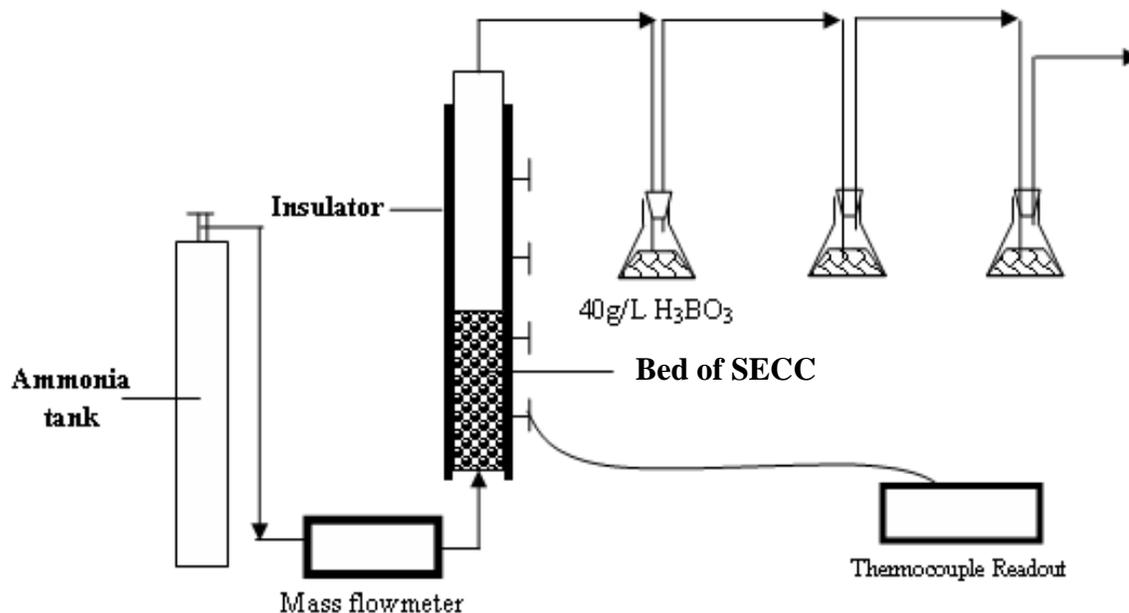

Figure 4.0 Schematic diagram of experimental setup for ammonia adsorption in a packed bed reactor

4.1.5 Spectroscopic characterization

Attenuated Total Reflection Fourier Transform Infrared, (ATR-FTIR), spectroscopy is a versatile and powerful technique for infrared sampling that requires minimal or no sample preparation for rapid analysis. ATR method makes it possible to press a sample onto the ATR crystal at high pressures which allows a more uniform penetration by the evanescent radiation and a higher degree of spectral reproducibility. No grinding is necessary in this case for solid sample therefore facilitating ease and speed in sample

preparation. For the purposes of acquiring a semi-quantitative data, 10.0 mg of material were weighed and a FTIR Model M-2000 (Midac Corporation, Costa Mesa, CA, USA) equipped with a diamond ATR cell with a circular surface of 3 mm diameter and three internal reflections was used for collection of spectra of each sample. Spectra were collected between 4000–700 cm^{-1} at a 4 cm^{-1} resolution with 64 scans each.

4.1.6 TGA-DSC Characterization

The SDT Q600 Simultaneous DSC-TGA Analyzer (TA Instruments, Inc) was used in this study. This instrument permits simultaneous monitoring of both heat and mass changes. It incorporates a null deflection thermobalance capable of weighing sub-milligram quantities and a chromelalumel heat flux DSC head. The instrument was used without further modification except that the secondary gas, ammonia was introduced at 20 ml/min. The DSC was first calibrated by measuring the heat of fusion of a sample of zinc. The system's microbalance is composed of two crucibles (90μL), one of these crucibles remains empty (it is the reference). The other one is filled with the adsorbent sample. A 20.0mg portion of the sample was placed in an aluminum crucible of size 90μL after both the reference and the sample crucible was tarred. The experiment was conducted under isothermal condition of 25 ^{o}C at a heating rate of 5 ^{o}C/min. During the run, the ammonia gas was introduced after 60 min run of the experiment. During the adsorption process, the sample mass increases till the steam exploded corn cob reaches saturation then gas supply was interrupted. The DSC signal and the sample mass were recorded simultaneously.

4.2 Results and Discussion

4.2.1 Dynamic Ammonia adsorption

The study of adsorption of ammonia on both raw and steam exploded corn cob was carried out in a custom made packed bed reactor. The amount of ammonia adsorbed was determined by weighing the bed before and after the adsorption. The adsorption capacity was found by dividing the amount of ammonia adsorbed by the amount of steam exploded corn used for the adsorption experiment. For the various adsorption capacity calculated, it is evident that the steam explosion pretreatment enhanced the ammonia removal capacity of the corn cob as shown in Table 4.0. Figure 4.1 shows that treating corn cob at 200 ^{o}C for 5 min increased the ammonia removal capacity by a factor of 3.5 whilst at 220 ^{o}C for the residence time of 2 min, the adsorption capacity increased 5.7 times. Similar trend was observed when samples were treated at different residence time interval (Figure 4.2).

Table 4.0 Adsorption capacity and pH of SECC at different severities

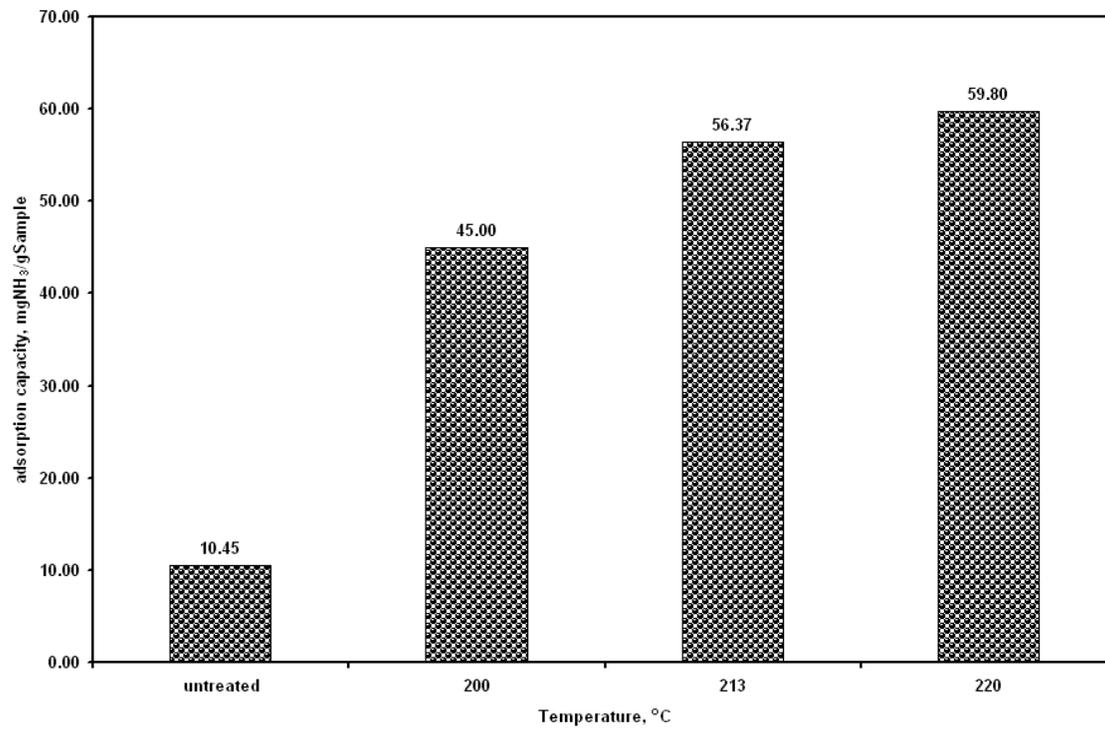| Sample #	Temperature, oC	Residence time, min	Severity factor	pH	Adsorption capacity, mg/gSample
1	untreated	untreated		4.86	10.45
2	200	1	2.94	4.60	37.00
3	200	3	3.42	4.09	41.58
4	200	5	3.64	4.04	45.00
5	213	1	3.33	4.30	47.58
6	213	3	3.80	3.97	56.35
7	213	5	4.03	3.87	56.37
8	220	2	3.83	3.78	59.80

Figure 4.1 Adsorption capacity of ammonia steam exploded corn cob at different temperatures
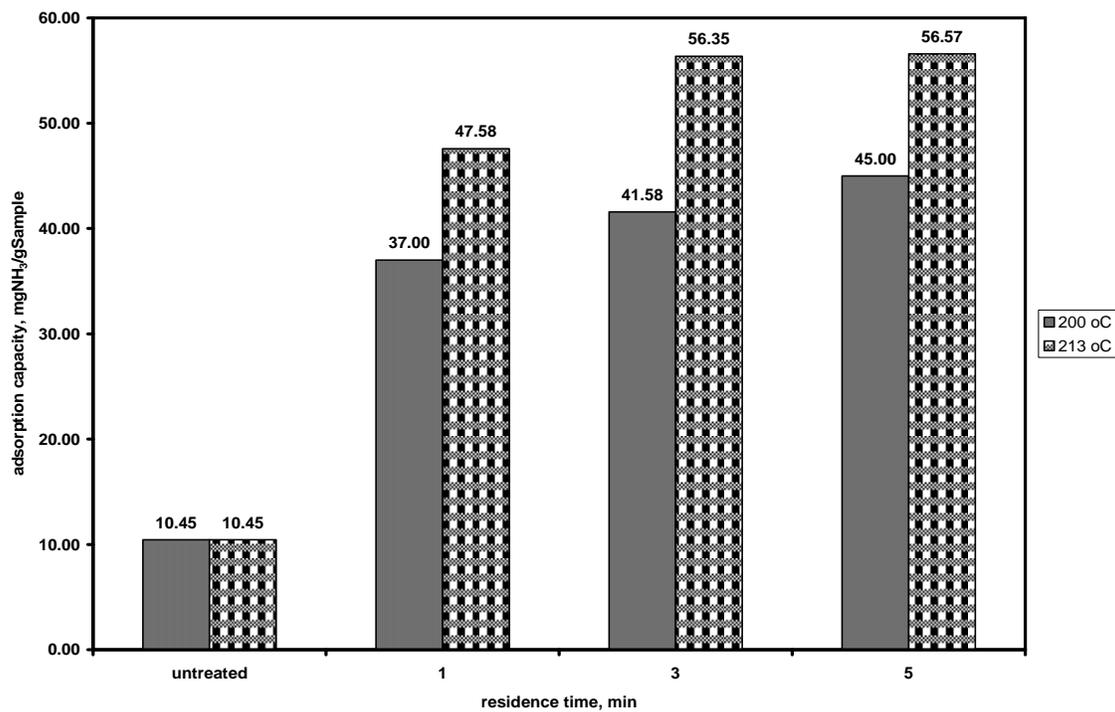
Figure 4.2 Adsorption capacity of ammonia on steam exploded corn cob at different residence time

4.2.2 Spectroscopic Characterization

The FT-IR spectra of RCC and SECC are shown in Figures 4.3 and 4.4 respectively. The spectra of RCC and SECC were measured within the range of 500–4000 cm^{-1} wave number. The FT-IR spectra of RCC and SECC displayed a number of absorption peaks, indicating the complex nature of the studied adsorbents. The FT-IR spectra of RCC and SECC displayed a number of absorption peaks, indicating the complex nature of the studied adsorbents. The RCC spectra showed peaks at 3334 cm^{-1} assigned as O–H stretch band indicating the presence of hydroxyl groups. A peak at 1716 cm^{-1} was assigned to carbonyl stretch (C=O) which is attributed to the acetyl and ester groups of the hemicelluloses or from the ester linkage of carboxylic groups (Adib and Bandosz, 2000 and Sun et al., 2001). The absorption at 1511 cm^{-1} is a characteristic peak for lignin due to the C=C stretching vibrations of the aromatic rings present in lignin. Bands between 1156 and 1031 cm^{-1} were typical of C-O stretch deformation bands of cellulose and residual hemicelluloses. A small sharp band at 897, 831 and 666 cm^{-1} corresponds to the ring frequency which is characteristic of β-glycosidic linkages between the sugar units (Gupta et al., 1987).

In order to test the ammonia removal capacity of RCC, IR was conducted on the sample from the dynamic adsorption studies. Evident in Figure 4.3 is the disappearance of the carboxylic functional group peak at 1716cm^{-1} and formation of a new peak observed at 1593cm^{-1}. The presence of this new peak supports the hypothesis of the formation of a complex between ammonia and RCC.
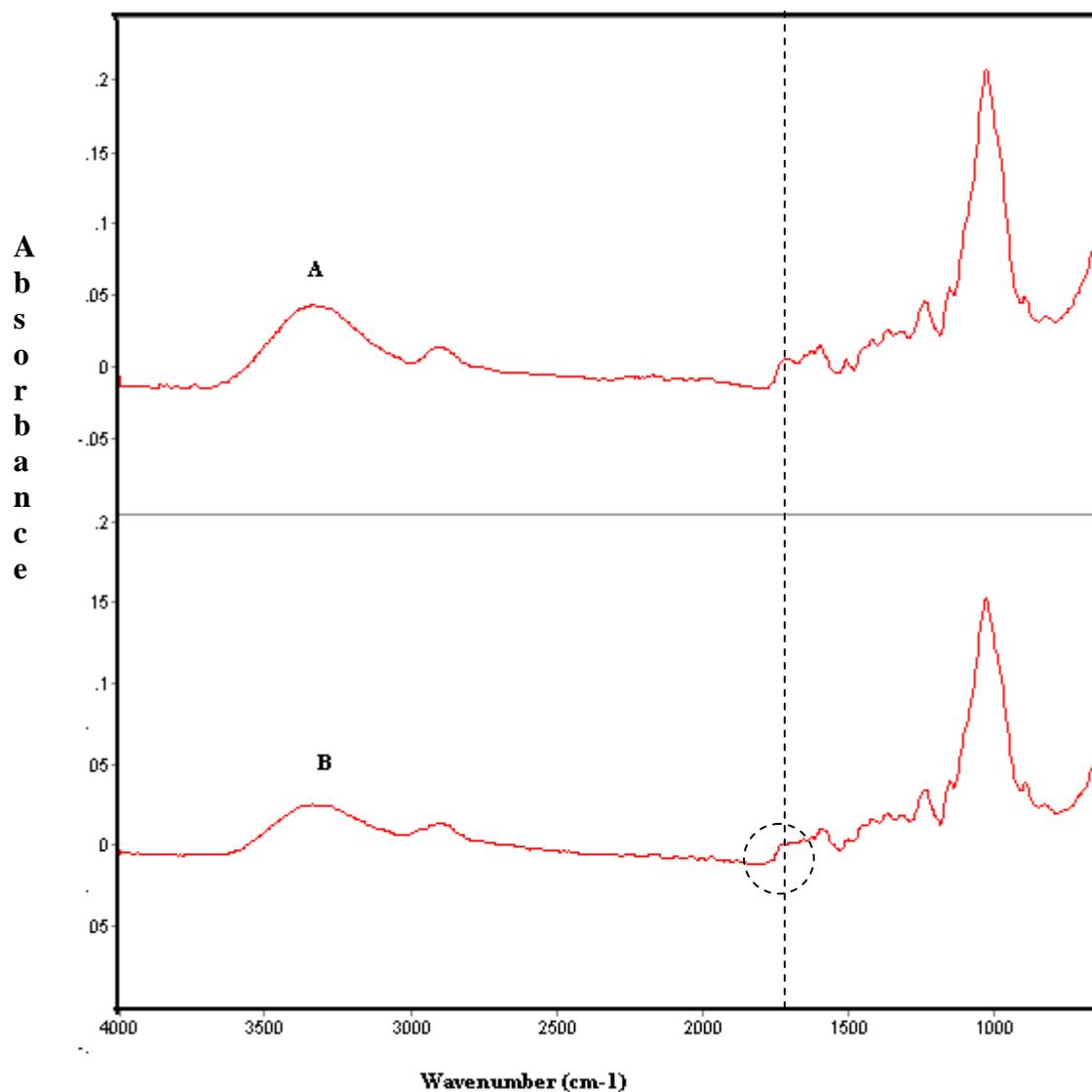
Figure 4.3 FTIR spectra of raw corn cob (A) and ammonia adsorbed on raw corn cob (B)

Upon steam exploding raw corn cob, a completely new structure was formed as depicted in Figure 4.4 below. The steam exploded corn cob showed a noticeable difference since the 1716 cm^{-1} peak changed to a sharper peak at 1700 cm^{-1} which is indicative of a shift toward a more acidic structure. Treating SECC with ammonia showed a similar trend like the RCC sample. The only difference is the formation of the new peak at 1584 cm^{-1}. To test whether the reaction lead to physical or chemical bond, a desorption test was

conducted. It is evident in Figure 4.5 that a new substance was formed when SECC was treated with ammonia. These changes happened in the range of stretching vibrations of C=O and are caused by ammonia chemisorption on the raw and steam exploded corn cob surfaces. Tables 4.1 and 4.2 present the fundamental peaks of the RCC, SECC and ammonia adsorbed samples respectively.
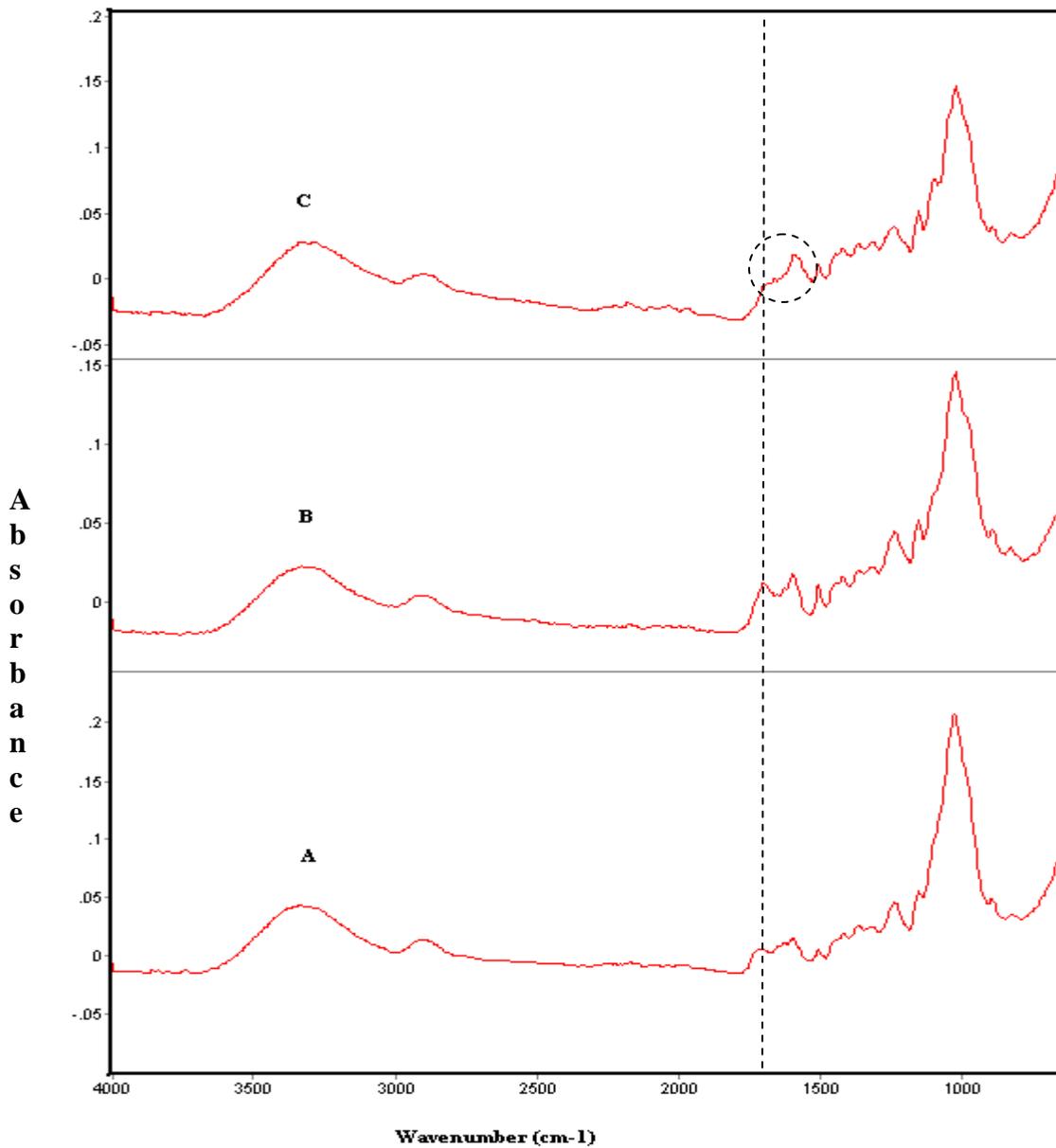

Figure 4.4 FTIR spectra of raw corn cob (A) and Steam exploded corn cob (B) and ammonia adsorbed on steam exploded corn cob (C)
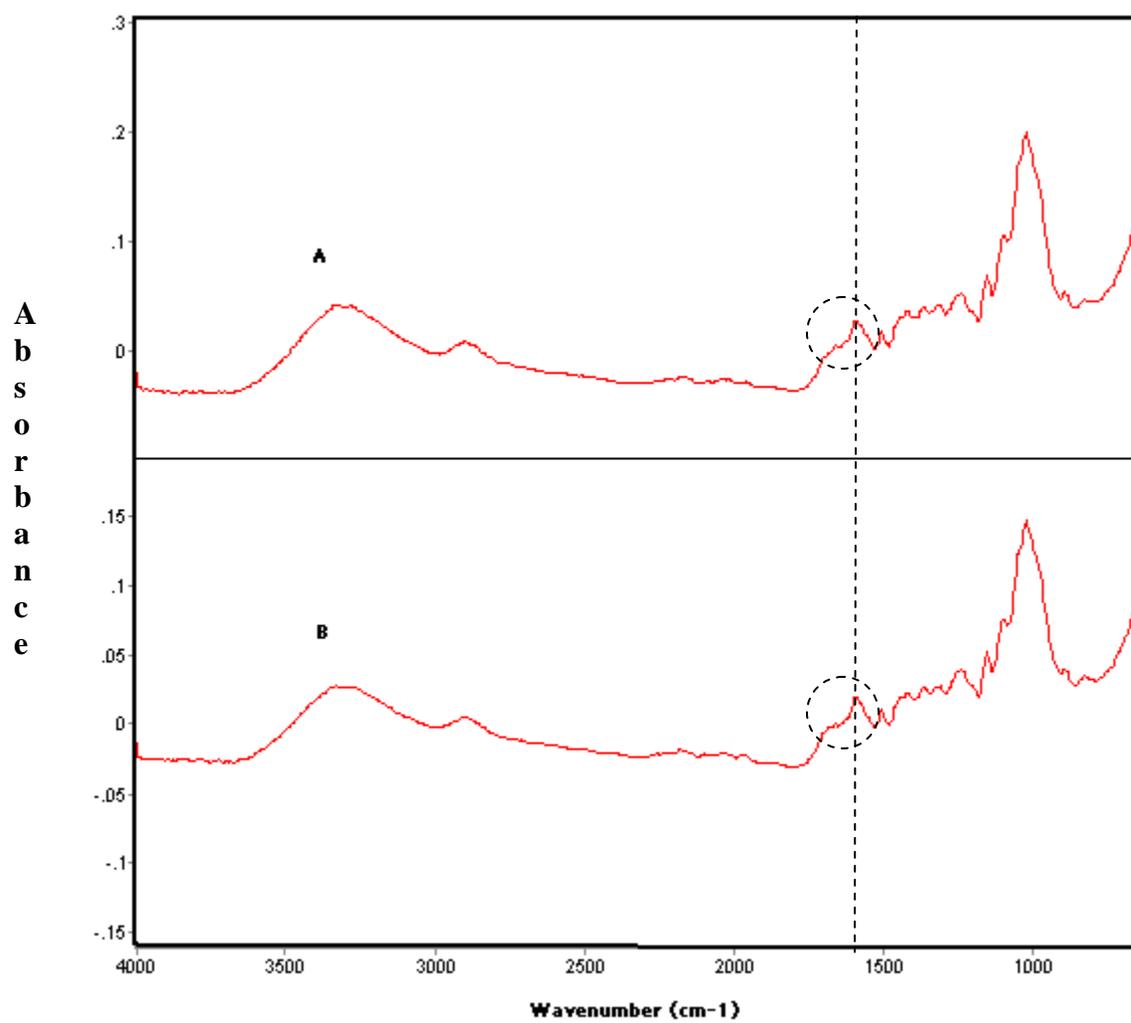
Figure 4.5 FTIR spectra of ammonia adsorbed on steam exploded corn cob (A) and ammonia desorbed from steam exploded corn cob (B)

Table 4.1 Summary of IR of RCC and SECC

RCC		SECC			Assignment	References
Band position, cm^{-1}	Assignment	SECC at 200 ^{o}C for 5 min	SECC at 213 ^{o}C for 5 min	SECC at 220 ^{o}C for 2 min		
3334	O-H stretch	3333	3327	3327	O-H stretch	Shishir et al., 2007
2910	C-H	2902	2902	2902	C-H	Umesh et al., 2007
1716	C=O carbonyl stretch	1701	1701	1700	C=O carbonyl stretch	Sun et al., 2001
1632	C=C stretch	ND	ND	ND	-	Clave et al., 2003
1600	C=C (aromatic ring	1600	1600	1600	C=C (aromatic ring)	
1511	C=C (aromatic ring)	1511	1511	1511	C=C (aromatic ring)	Shishir et al., 2007
1156	C-O stretch	1159	1159	1159	C-O stretch	
1101	ND	1101	1102	1102	Absorption band for xylan	
1031	C-O stretch deformation	1030	1028	1028	C-O stretch deformation	
897	β-glycosidic ethyl linkages between sugar units	897	897	897	β-glycosidic ethyl linkages between sugar units	
832		831	831	831		
664		660	660	660		

Note: ND – Not Detected

Table 4.2 Summary of IR spectra of RCC and SECC reacted with ammonia

RCC		RCC + Ammonia	SECC	SEEC + Ammonia
Band position, cm^{-1}	Assignment	Band position, cm^{-1}	Band position , cm^{-1}	Band position cm^{-1}
3334	O-H stretch	3333	3327	3327
2910	C-H	2902	2910	2902
1716	C=O carbonyl stretch	Disappeared	1701	Disappeared
1632	C=C stretch		ND	ND
1600	C=C (aromatic ring)	Disappeared	C=C (aromatic ring)	Disappeared
1593	-COONH$_4$	Carboxylic salt	-COONH$_4$	Carboxylic salt
1511	C=C (aromatic ring)	1511	1511	1511
1156	C-O stretch	1159	1159	1159
1101	ND	1101	1102	1102
1031	C-O stretch deformation	1030	1028	1028
897	β-glycosidic ethyl linkages between sugar units	897	897	897
832		831	831	831
664		664	660	660

The disappearance of band at 1700 cm^{-1} and 1716 cm^{-1} is caused by the reaction between NH$_3$ and RCC and SECC. Because corncobs are natural products consisting primarily of cellulose, hemicelluloses, and lignin (Hon et al., 1996), main active sites for ammonia interaction with the corn cob will be carboxylic group. This functional group is very predominant in hemicelluloses. Upon reaction with ammonia with the surface of SECC,

an ammonium salt of carboxylic acids is likely to be formed. In order to investigate the above, IR analysis was conducted on ammonium formate, ammonium acetate and ammonium citrate. Their IR spectra are shown in Figures 4.6, 4.7 and 4.8.
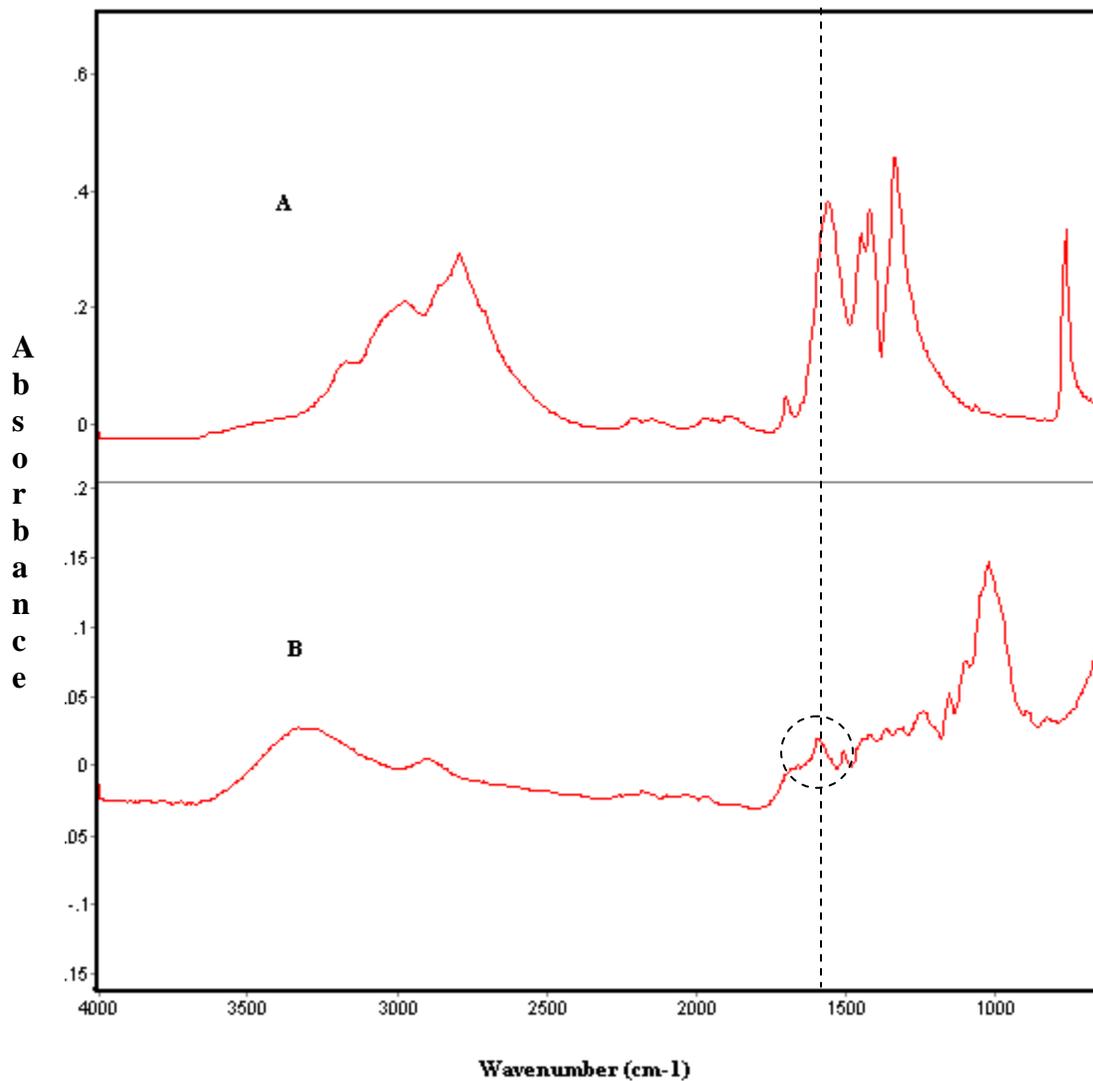

Figure 4.6 FTIR spectra of ammonium formate (A) and ammonia adsorbed on steam exploded corn cob (B)
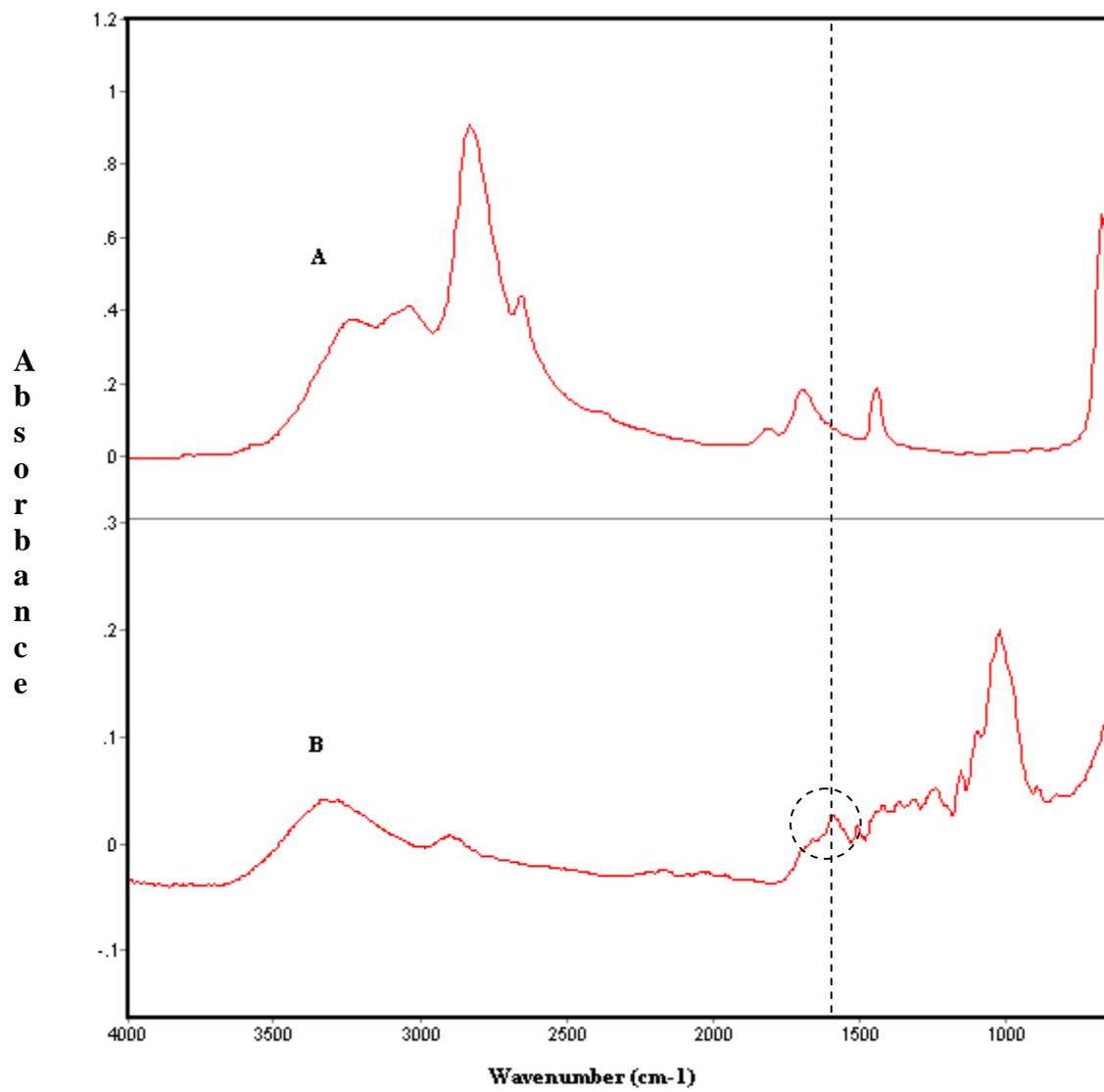
Figure 4.7 FTIR spectra of ammonium Acetate (A) and ammonia adsorbed on steam
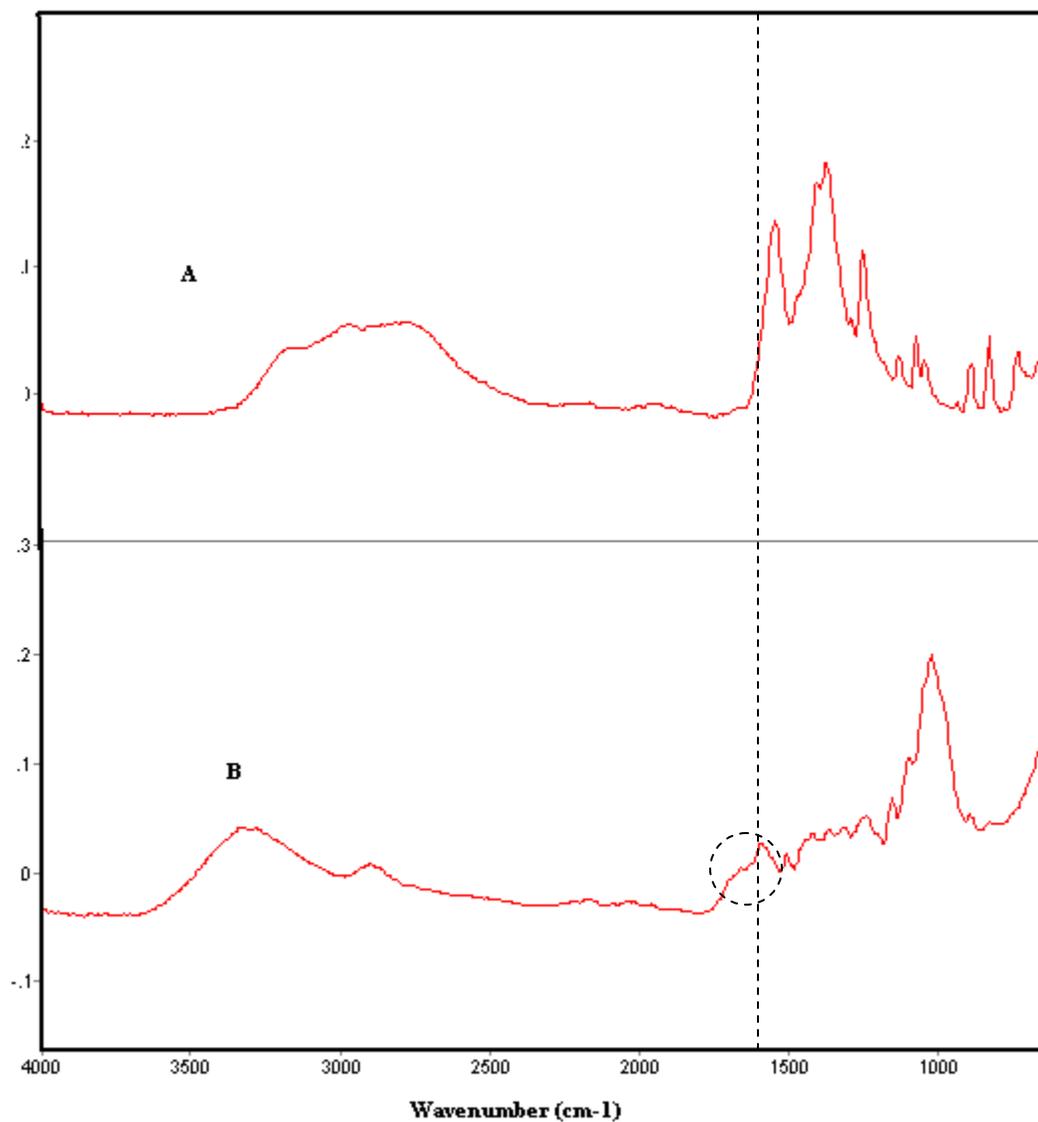
exploded corn cob (B)

Figure 4.8 FTIR spectra of ammonium Citrate (A) and ammonia adsorbed on steam

exploded corn cob (B)

The FTIR spectra scans taken for ammonium formate, ammonium acetate and ammonium citrate showed peaks at 1562, 1556 and 1549 cm^{-1} respectively. Comparing FTIR spectra of ammonium formate, ammonium acetate and ammonium citrate with the ammonia adsorbed SECC, it could be inferred that formic acids is the likely acids reacting with ammonia that resulted in the formation of a completely new absorption

band at 1584 cm^{-1}. Although this value deviates from the actual value of 1562 cm^{-1}, the possible explanation could be that, formic acid formed as result of the steam explosion was bounded to SECC surface. However, further study and analysis need to be done to substantiate the above claim.

The semi-quantitative analysis indicated that higher severities influence the amount of carboxylic group available for ammonia adsorption. It is evident in Figures 4.9 and 4.10, the amount of aromatic functional group content remained fairly constant after steam exploding the material at higher temperatures.
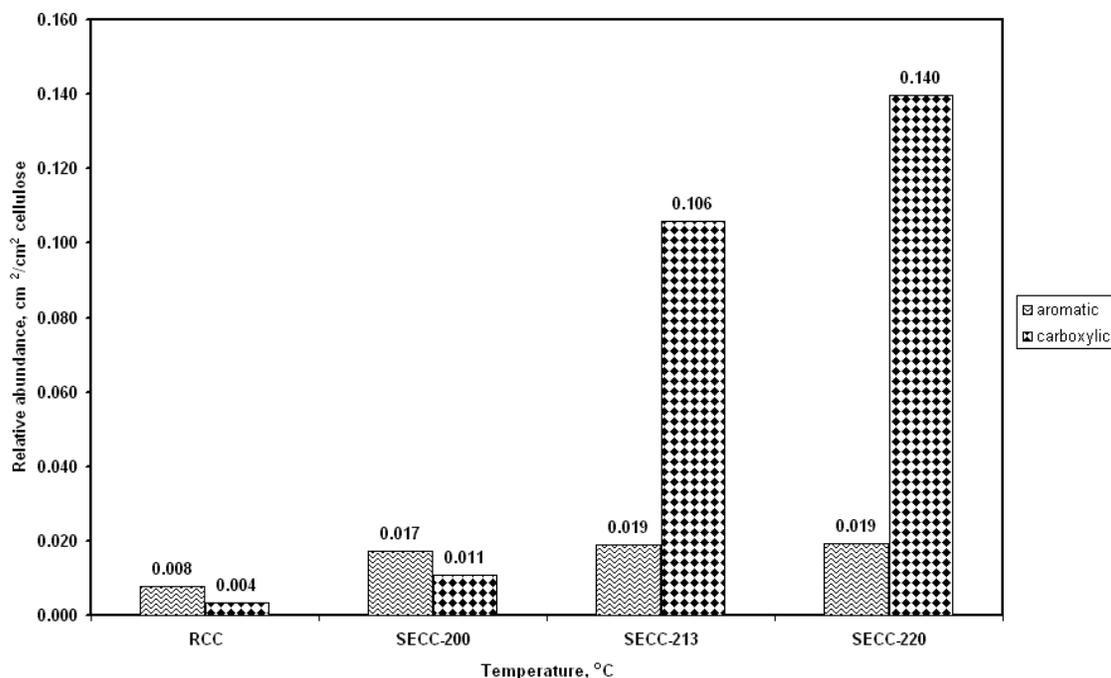

Figure 4.9 Relative abundance of functional groups in RCC and SECC. SECC-200, SECC-213, and SECC-220 are steam treated at 5, 5 and 2 min respectively
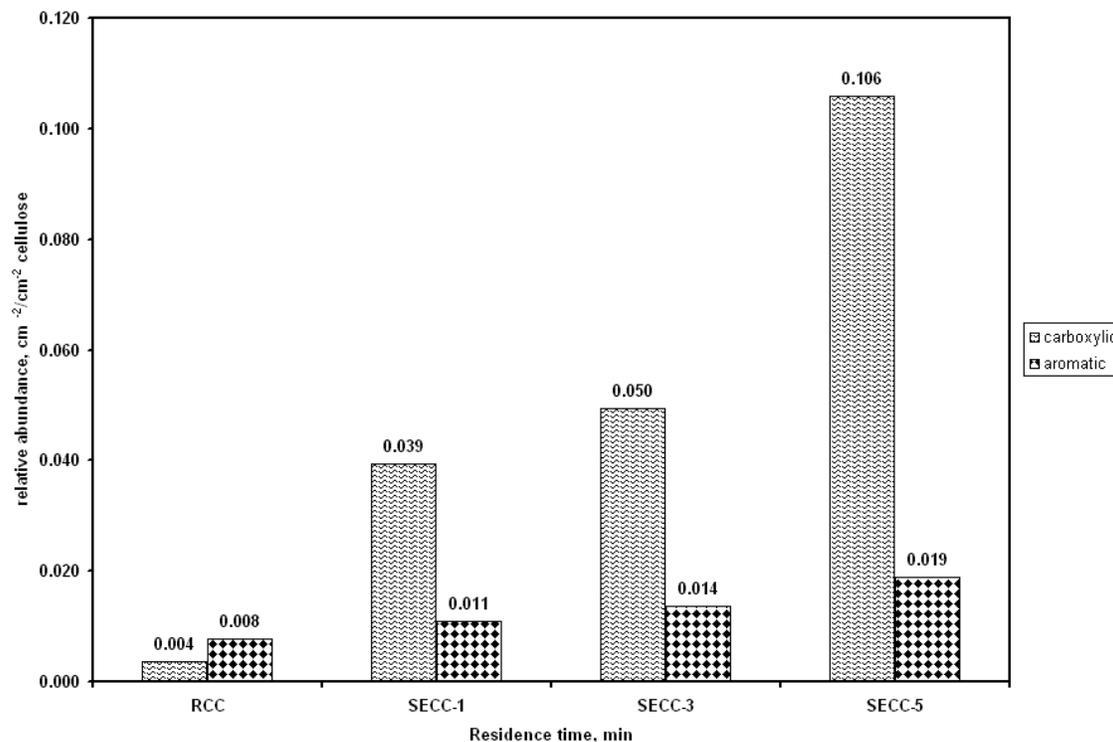
Figure 4.10 Relative abundance of functional groups in RCC and SECC at 200 oC.

SECC-1, SECC-3 and SECC-5 are residence time of 1, 3 and 5 min respectively

4.2.3 TGA Characterization

The TGA weight loss-curves for the both steam exploded corn cob and ammonia adsorbed steam exploded corn cob are shown in Figure 4.12. The result shows that both samples remained fairly stable between 25 to 100 $^{\circ}$C. Data shown in Figure 4.11 indicated clearly that only a small mass loss in the ammonia adsorbed SECC occurred within 100 to 200 $^{\circ}$C. This could be explained as strong bond formed between the SECC and ammonia. After 200°C, both SECC and ammonia adsorbed SECC seem to degrade probably due to the high temperature of operation.
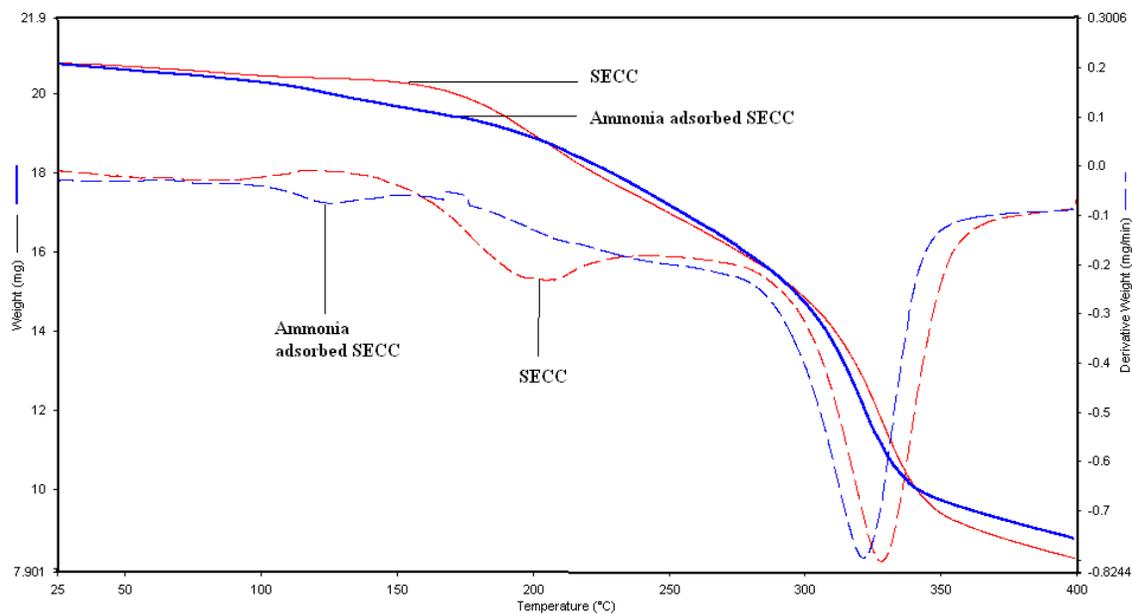
Figure 4.11 TGA weight loss-curve for steam exploded corn cob and ammonia adsorbed

sample

4.2.4 DSC Characterization

The heat of adsorption of a given adsorption process is one of the most useful parameters in surface science studies. There are essentially three methods for experimental determination of the heat of adsorption:

1. calculation from adsorption equilibrium data;

2. calculation from desorption kinetics data; and

3. calorimetric measurement. The most reliable method of determining the heat of adsorption is by the calorimetric method.

The calorimetric determination of heat of adsorption does not require any model of the surface process and measure the heat directly. This method of heat adsorption determination is capable of handling both reversible and irreversible processes.

This method was used for the determination of heat of adsorption of ammonia on steam exploded corn cob at $25^{o}C$. The adsorption TGA-DSC curve is shown in Figure 4.12.

First, the experiment was conducted under isothermal condition for 60 min before introducing the ammonia gas after a constant reaction temperature of 25 $^{\circ}$C was attained. When the ammonia gas was passing through the steam exploded corn cob, both weight increase and heat release were observed from the adsorption of ammonia on the steam exploded corn cob as shown in Figure 4.13. The adsorptive saturation was achieved after 180 min. The enthalpy of adsorption was determined from the peak area in Figure 4.13 by integration. The estimated heat of adsorption was 33.20 J/g of adsorbent (~33.00 kJ/mol of ammonia). The heat of adsorption of ammonia on activated carbon is typically around 25.12 to 27.21 kJ/mol (Boehm et al., 1959 and Avgul and Kiselev, 1970). By contrast, according to Bastick et al (1977), the heats of ammonia adsorption on carboxyl groups was shown to be between 87.92 and 62.80 kJ/mol. The magnitude of the heat of adsorption gives an idea about the type of adsorption which is mainly physical or chemical. Also, Nollet et al. (2003) classified the type of adsorption based on the activation energy; physisorption processes usually have energies in the range of 5-40 kJ/mol while higher activation energies 40-800 kJ/mol suggests chemisorption. On the basis of the low heat of adsorption, it is reasonable to assume that the adsorption type could be physisorption. Meanwhile, the IR study clearly shows chemisorption. It is likely both ammonia adsorption on SECC is a combination physisorption and chemisorption. It will be suggested that further test be carried to substantiate the above claim.
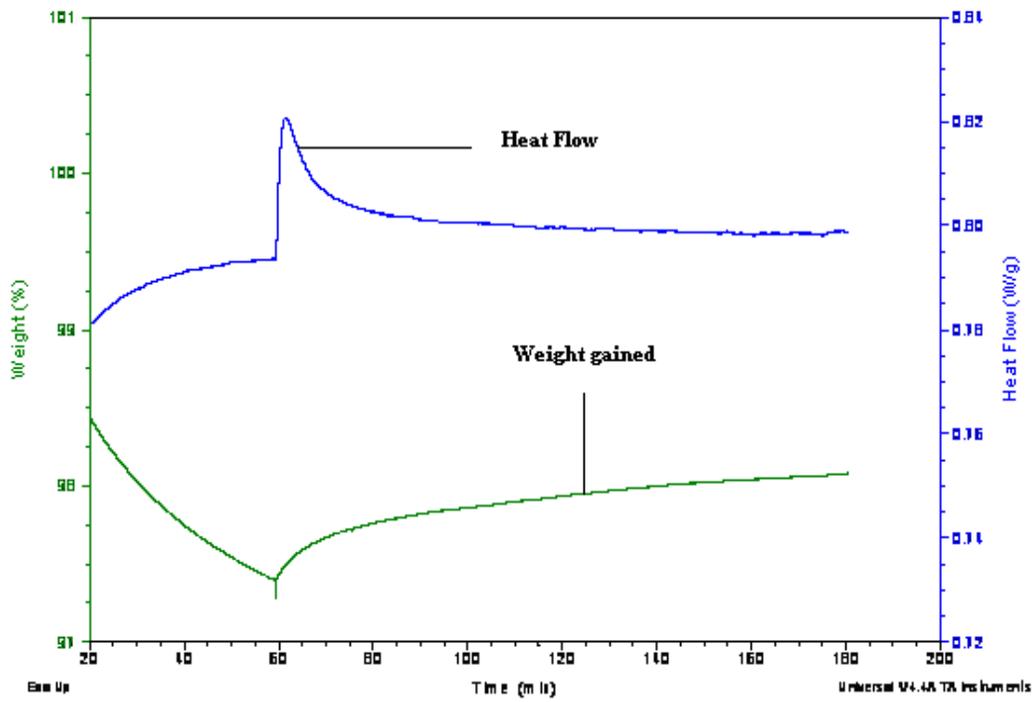
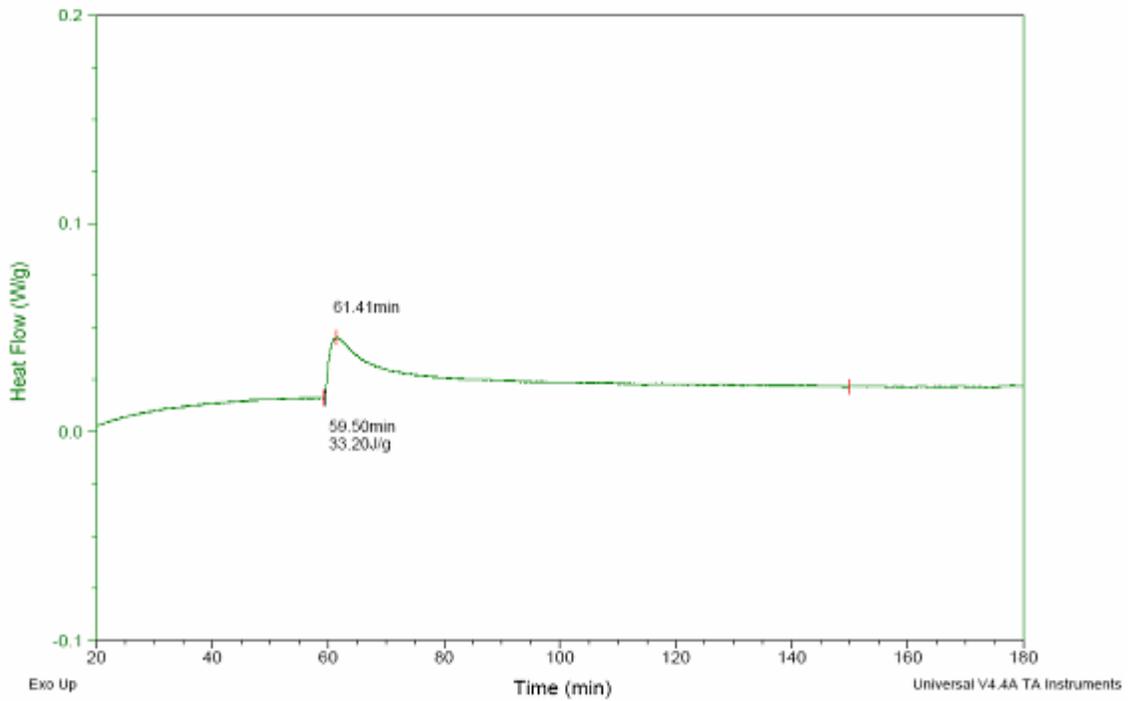Figure 4.12 TGA-DSC curve of ammonia adsorption on steam exploded corn cob

Figure 4.13 Heat of Adsorption of Ammonia adsorption on steam exploded corn cob

4.3 Conclusions

In this work the adsorption of ammonia has been showed using a packed bed reactor. The highest adsorptive capacity was recorded for steam exploded corn cob at 220 ^{o}C at 2 min exposure. The packed column studies showed that the maximum adsorption capacities of the raw corn cob (RCC) and the steam exploded corn cob (SECC) were respectively 10.45 mg NH_3/g RCC and 59.80 mg NH_3/gSECC.

The FTIR bands in the region between 1500 and 2000 cm^{-1} showed a considerable difference between RCC and SECC. When SECC was treated with ammonia, the carboxylic functional group peak at 1700cm^{-1} was reduced and a new peak was observed at 1584 cm^{-1}. A similar trend was observed for the RCC when it was treated with ammonia. In this case, the disappearance of the carboxylic functional group peak at 1716 cm^{-1} and formation of a new peak at 1593 cm^{-1}. The presence of these new peaks supports the hypothesis of the formation of product from the ammonia and RCC and SECC. The adsorption, desorption test and heat of adsorption (33.0 kJ per mole of NH_3) results suggested combined physisorption and chemisorption of ammonia on SECC but chemisorption was found to play an important role in ammonia removal.

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CHAPTER FIVE

SUMMARY AND RECOMMENDATIONS

The packed column studies showed that the maximum absorption capacities of the raw corn cob (RCC) and the steam exploded corn cob (SECC) were respectively 10.45 mg NH_3/g RCC and 59.80 mg NH_3/gSECC. However, the titration of the slurries with a NH_4OH showed that the capacity of the SECC was 14.4 times that of RCC. The large difference between the packed column (SECC/RCC = 5.7) and the slurry titration (SECC/RCC = 14.4) was probably because: (1) the initial ammonia reaction products blocked the pores of the SECC and reduced diffusion into the pore structure; (2) the ammonia gas flow rates were too high and therefore the gas did not penetrate the pores; (3) the gas contact time was below the equilibrium value; and (4) since interior pore surface area is usually larger than the external surface area of a particle, it appears the low column SECC/RCC ratio is due to reactions on the SECC particle surface whereas the slurry result was a combination of both.

The simple addition of small quantities of $Al_2(SO_4)_3.xH_2O$ and $Fe_2(SO_4)_3.xH_2O$ to SECC Improved the acidity of the mixture, whereas the impregnation of the SECC with $Al_2(SO_4)_3.xH_2O$ and $Fe_2(SO_4)_3.xH_2O$ reduced the acidity of SECC and its ammonia removal capacity. In order to improve the impregnation of the acidic salts the future work will be to add the salts to the raw corn cob during the steam explosion.

When IR spectroscopic analysis was conducted on RCC and SECC, the bands both samples showed a considerable difference in the region 1500 and 2000 cm^{-1}. When SECC was treated with ammonia, the carboxylic functional group peak at 1700 cm^{-1} was reduced and a new peak was observed at 1584 cm^{-1}. A similar trend was observed for the

RCC when it was treated with ammonia. In this case, the disappearance of the carboxylic functional group peak at 1716 cm^{-1} and led to the formation of a new peak observed at 1593 cm^{-1}. The presence of these new peaks supports the hypothesis of the formation of a complex between ammonia and RCC and SECC. The adsorption, desorption test and heat of adsorption (33.0 kJ per mole of NH$_3$) results suggested combined physisorption and chemisorption of ammonia on SECC but chemisorption was found to play an important role in ammonia removal.

In order to address the discrepancies between the batch studies and the packed column studies it is recommended that following studies should be carried in future:

1. the effect of gas flow rate should be investigated since a low flow will allow full equilibration of ammonia in the packed bed reactor. Several flow rates should be tested and the optimum level of feeding the gas determined.

2. to address the issue of low adsorption capacity due diffusion limitation, different particle sizes should be selected and the optimum particle size determined, and finally

3. pore size distribution should be conducted on the ammonia adsorbed SECC to ascertain whether the pore size decreased as result of the blockage of the pore during the adsorption process.

The results from this study show that we have successfully produced an adsorbent from a corn cob, a biodegradable material which could be potentially used to remove NH$_3$ from various emission sources. Though the results from this study showed that SECC is an effective adsorbent for ammonia removal, it could also serve as good adsorbent for the

removal for other air pollutant. It is therefore recommended that further studies be carried out on the effectiveness of SECC on other air pollutant.

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