ABSTRACT

PYROLYSIS OF DE-INKED PAPER SLUDGE FOR ADSORBENT SYNTHESIS

by Na Qin

De-inked paper sludge (DPS) was pyrolyzed at 600°C, 750°C and 900°C in nitrogen to synthesize carbon-calcium-based adsorbents. The performance of the synthesized adsorbents for the gas-phase adsorption of elemental mercury (Hg), sulfur dioxide (SO₂), and isoamyl acetate (IAA) vapor was investigated, and the performance was compared to that of commercially available activated carbon (BPL, Calgon Carbon Corporation). The physical and chemical properties of the pyrolyzed DPS and BPL were characterized to assess their chemical and physical differences, and those differences were used to hypothesize reasons for differences in their adsorption performance for the selected test compounds (elemental Hg, SO₂ and IAA). Characterization of the adsorbents was conducted using BET surface area, X-ray diffraction, TGA, scanning electron microscopy, electron dispersion spectroscopy, and FTIR. Gas chromatography was used to analyze IAA collected throughout the adsorption process. Adsorption capacities of pyrolyzed DPS and BPL were investigated in different experimental conditions (temperature, steam, etc.).
PYROLYSIS OF DE-INKED PAPER SLUDGE FOR ADSORBENT SYNTHESIS

A Thesis
submitted to the faculty
of Miami University in partial fulfillment of
the requirements for the degree of

Master of Science
Department of Paper and Chemical Engineering

by

Na Qin
Miami University
Oxford, Ohio
January 15, 2010

Advisor  Dr. Catherine Almquist

Reader  Dr. Lei Kerr

Reader  Dr. Doug Coffin
TABLE OF CONTENTS

Chapter 1 ......................................................................................................................... 1
Introduction ....................................................................................................................... 1
  1.1 Disposal of Industrial Waste .................................................................................... 1
  1.2 Beneficial Uses of DPS .......................................................................................... 2
  1.3 Pyrolysis of DPS .................................................................................................... 3
  1.4 Adsorption ............................................................................................................. 3
  1.5 Adsorbents ............................................................................................................ 5
  1.6 Activated Carbon Adsorption .................................................................................. 7
    1.6.1 Elemental Mercury Adsorption ....................................................................... 7
    1.6.2 Sulfur Dioxide Adsorption ............................................................................. 9
    1.6.3 VOCs Adsorption ............................................................................................ 10

Chapter 2 ........................................................................................................................ 12
Research goals and objectives ......................................................................................... 12

Chapter 3 ........................................................................................................................ 13
Experimental design ........................................................................................................ 13

Chapter 4 ........................................................................................................................ 14
Experimental methods ...................................................................................................... 14
  4.1 Adsorbent Preparation ......................................................................................... 14
  4.2 Adsorbent Characterization .................................................................................. 14
    4.2.1 X-ray Diffraction ............................................................................................ 18
    4.2.2 Brunauer Emett Teller .................................................................................. 19
    4.2.3 Scanning Electron Microscopy ....................................................................... 21
    4.2.4 Energy Dispersive Spectrometry ................................................................... 21
    4.2.5 Thermogravimetric Analysis ......................................................................... 21
    4.2.6 Fourier transform spectroscopy ..................................................................... 22
  4.3 Adsorbent Performance ......................................................................................... 24
    4.3.1 Mercury adsorption test set-up .................................................................... 24
4.3.2 Sulfur dioxide adsorption test set-up.................................24
4.3.3 Isoamyl Acetate adsorption test set-up.................................25

Chapter 5..................................................................................28
Results and discussion.................................................................28
  5.1 Adsorbent characterization.....................................................28
    5.1.1 BET Surface Analysis.....................................................28
    5.1.2 X-ray Diffraction Analysis..............................................30
    5.1.3 Scanning Electron Microscopy........................................31
    5.1.4 Energy Dispersive spectrometry Analysis..........................33
    5.1.5 Thermogravimetric analysis..........................................34
    5.1.6 Fourier transform spectoscopy........................................35
  5.2 Adsorption Performance......................................................36
    5.2.1 Adsorption for elemental Mercury....................................36
    5.2.2 Adsorption for Sulfur Dioxide........................................40
    5.2.3 Adsorption for VOCs...................................................45

Chapter 6..................................................................................47
Conclusions and recommendations.............................................47

Reference..................................................................................50
LIST OF TABLES

Table 1: Distribution of Current Disposal Practices [1]………………………………….2
Table 2: Comparison of metals content of DPS…………………………………………17
Table 3: Gas Chromatography calibration………………………………………………26
Table 4: BET surface area of adsorbents used in this study……………………………..29
Table 5: Table of Elementary Analysis of pyrolyzed DPS by Energy Dispersive
Spectrometry analysis……………………………………………………………………34
Table 6: Mercury Adsorption capacity .................................................................37
Table 7: SO₂ adsorption capacity y.................................................................44
Table 8: IAA Adsorption capacity at room temperature.................................46
LIST OF FIGURES

Figure 1: Material flow in pulp and paper industry ................................................. 1
Figure 2: Isoamyl Acetate molecular formula ................................................................. 5
Figure 3: Schematic of DPS trapped between two plugs of quartz wool in tube...14
Figure 4: Schematic of the test system used for mercury adsorption performance ....24
Figure 5: Schematic of the test system used for Sulfur Dioxide adsorption performance.24
Figure 6: Schematic of the test system used for Isoamyl Acetate adsorption performance ................................................................. 25
Figure 7: IAA adsorption system calibration curve ....................................................... 26
Figure 8: Pore size distribution of pyrolyzed DPS, BPL and Raw DPS ................. 29
Figure 9: XRD spectra of pyrolyzed DPS compared to that for BPL .................. 31
Figure 10: SEM images of Pyrolyzed DPS and BPL .................................................. 32
Figure 11 Light microscope images of raw DPS ....................................................... 33
Figure 12: TGA curves of different temperature pyrolyzed DPS and BPL .......... 35
Figure 13: FTIR curves of each type of pyrolyzed DPS and BPL ....................... 36
Figure 14: Affect of pyrolysed temperature under 30°C for Hg adsorption ............ 37
Figure 15: Affect of Hg adsorption temperature for pyrolyzed DPS ................. 39
Figure 16: Affect of pyrolysis temperature in SO₂ adsorption ......................... 41
Figure 17: Affect of adsorption temperature of SO₂ by pyrolyzed DPS and BPL ................................ ................................................................. 42
Figure 18: Affect of steam in SO₂ adsorption at 100°C ............................................ 44
Figure 19: Affect of temperature of steam in SO₂ adsorption ..........................45
Figure 20: The effect of pyrolysis for IAA adsorption ........................................ 46
ACKNOWLEDGEMENTS

I would like to express my gratitude to the people who supported me and help me in the completion of the thesis. First of all, I would like to express my immense thanks to my academic advisor, Dr. Catherine Almquist for her consistent guidance and support though out my thesis and research. The thesis would not be completed without her inspiration and comments. I would like to thank Dr. Douglas Coffin and Dr. Lei Kerr for their thorough reviews and suggestions. I would like to thank Dr. Lee, Joo-Youp (University of Cincinnati) for his help in mercury adsorption system.

I would also like to thank Dr. Edelmann, Matt Duley, John Morton, Mr. Doug Hart and Ms. Laurie Picadio for their assistance in characterization techniques and several processes. Also, I would like to thank Paper and Chemical Engineering department faculty members for their continuous support throughout the course, and all graduate students for their cooperation and kindliness.
1.1 Disposal of Industrial Waste

Industrial waste, or residues, from pulp and paper mills are discharged through air, water and land, as shown in the simple schematic in Figure 1. Waste is emitted to air from stacks and fugitive emissions (leaks, spills); to water in the form of treated effluents; and to the land in the form of sludge and solid waste. In the last two decades, emissions by pulp and paper mills to air and water have been significantly reduced. In many cases, the water being discharged is cleaner than the water taken in by the mill. However, solid waste is still an economic and environmental burden for many mills.

![Material flow in pulp and paper industry](image)

Figure 1 Material flow in pulp and paper industry [1]

Table 1 summarizes the disposal methods used by pulp and paper mills for their solid waste. Noted is that the majority of mills landfill their solid waste, thus incurring annual disposal costs. Many mills incinerate their sludge to recover energy, although the high water content significantly lowers the heating value of the sludge. Landspreading of sludge waste is not done as often as landfilling and incineration due to the concerns regarding the presence of heavy metals and toxic organics in the sludge.
Table 1 Distribution of Current Disposal Practices

<table>
<thead>
<tr>
<th>Disposal method</th>
<th>Mills using method (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landfill</td>
<td>69</td>
</tr>
<tr>
<td>Incineration</td>
<td>21</td>
</tr>
<tr>
<td>Landspreading</td>
<td>8</td>
</tr>
<tr>
<td>Other methods</td>
<td>8</td>
</tr>
</tbody>
</table>

The disposal of de-inked paper sludge (DPS) is both an economic and environmental burden to recycled fiber paper mills. DPS contains waste fibers, fillers (e.g. calcium carbonate and titanium dioxide), organic chemicals and heavy metals from dyes, inks, and coatings. DPS is typically disposed in landfills, which may cost up to $30/ton. For example, Appleton’s West Carrollton, Ohio mill disposed nearly 100,000 tons of wet de-inked paper sludge in 2007, which is estimated to have cost the mill approximately $3,000,000.

1.2 Beneficial Uses of DPS

To remedy the economic and environmental burden of DPS disposal, beneficial uses of deinked paper sludge are being pursued by recycled fiber mills. Some successful beneficial uses of paper sludge include:

- land application of sludge to agricultural land [2]
- animal bedding materials [3]
- bioethanol and biofuel production [4]
- ceiling board material [5]

In a previous study (PCE 541 Pollution Prevention class project), my project team assessed beneficial uses of DPS for Appleton Papers. At that time, our team recommended that Appleton pursue animal bedding for small animals (e.g. pets, animals not for human consumption) as a beneficial use of their waste DPS.
As an extension to the class project, the pyrolysis of DPS was investigated in this study for the synthesis of sorbents that could be used for the capture of organic vapors, elemental mercury (Hg) and sulfur dioxide (SO$_2$) from gas streams.

1.3 Pyrolysis of DPS

Pyrolysis is a process by which organic substances are thermally decomposed in an oxygen-free atmosphere at temperatures up to 900°C. The reactions that take place during pyrolysis are endothermic, and include thermal cracking and condensation reactions. Pyrolysis is used for the production of charcoal and activated carbon. It is also used to produce chemicals from wood and other biomass materials.

In general, three types of products result from pyrolysis processes: [6]

1) A gaseous product, which contains mainly hydrogen, methane, carbon monoxide, carbon dioxide, and several other non-condensable gases in smaller concentrations.
2) A liquid product, which consists of a tar and/or oil and condensable organics that may include acetic acid, acetone, and methanol.
3) A solid product or char, which consists mainly of carbon and inorganic materials, including heavy metals.

In this study, only the solid product from the pyrolysis of DPS from Appleton Papers in West Carrollton was characterized and used as an adsorbent for elemental Hg, SO$_2$, and isoamyl acetate (IAA) vapors.

1.4 Adsorption

Adsorption is a process in which molecules (the adsorbates) are collected on the surface of an adsorbent (a solid material). Adsorption occurs because of the unsaturated
and unbalanced molecular forces presenting on the surface of solid material. While a solid surface is brought into contact with a fluid (gas or liquid), the molecules of the gas strike the surface of the solid. Some of these striking molecules stick to the solid surface and become adsorbed, while some others rebound back into the bulk fluid [5].

Adsorption is divided into two types: 1) chemical adsorption, and 2) physical adsorption. [7] Chemical adsorption results from chemical bond formation, which is relatively strong, between the adsorbent and the adsorbate in a monolayer on the surface. In physical adsorption, the adsorbate is bound to the surface by relatively weak Van der Waals force. Van der Waals force is similar to the molecular force of cohesion and condensation of vapors into liquid. Selectivity in physical adsorption relies on equilibrium and kinetics.

To achieve a sufficient adsorption capacity, an adsorbent must have a high surface area, supplying a highly porous surface with many small micropores. These micropores can be generated in many ways. Carbon sorbents are made by controlled burn of carbonaceous materials, such as sewage sludge and coal lignite. This process leads to a wide distribution of pore sizes. X-ray diffraction patterns of activated carbon show that it is amorphous because the randomly cross-linked network inhibits reorder of the structure while heating process. The surface area, dimensions, and distribution of the pores depend on the precursor and on the conditions of carbonization and activation. [8]

For a given adsorbent, the relative strength of adsorption of different adsorbate molecules depends on the relative magnitudes of the polarizability, dipole moment, and quadrupole moment of each. Considering the value of the three allows a qualitative prediction to be made of the relative strength of adsorption of the given molecules on a sorbent and determine the sorbent type (polar or nonpolar). In our study, mercury as a metal element is a non-polar molecule, thus the mercury physical adsorption mainly relies on van der Waals force. Sulfur dioxide is a polar molecule and thus has dipole-dipole forces as the intermolecular forces present between these molecules. IAA is a polar molecule; the molecular structure of IAA is shown in Figure 2. The polarizability is $14.35 \pm 0.510^{-24}$cm$^3$ and its boiling point $142 \degree C$. 
Adsorption efficiency decreases over time and eventually activated carbon will need to be replaced or reactivated. Isotherms are empirical relations which are used to predict how much gas can be adsorbed by activated carbon. The three most well known isotherms are the Freundlich, Langmuir and Linear. The Langmuir model is the first theoretically developed adsorption isotherm. An ideal Langmuir model is presented:

\[
\frac{q}{q_s} = \frac{bp}{1 + bp}
\]

where \(q_s\) is the saturation limit, \(q\) is absorbed phase concentration, \(b\) is an equilibrium constant and \(p\) is the particle pressure of adsorbate. The Langmuir model was originally developed to represent monolayer adsorption on an ideal surface, where \(q_s\) corresponds to the monolayer coverage. In this isotherm equation, the monolayer capacity should be temperature dependent. In physical adsorption, there is no dissociation of adsorbed species, it appears monolayer or multilayer phase; in chemical adsorption, because of involving dissociation, it is only limited to monolayer coverage.

1.5 Adsorbents

Activated carbon in the broad sense includes a wide range of processed amorphous carbon-based materials. Various raw materials as sources of activated carbon have been investigated. For example, activated carbon can be prepared from nutshells, peat, wood, lignite and coal.

Carbonaceous raw material could develop porosity and extend surface area by carbonization at a temperature below 900°C. During the heating process, a
microcrystalline structure is formed. A large surface and pore structure can develop, consisting of pores of different sizes and shapes. However, the high area carbon tends to lack material strength, which limits its practical applications.

Besides the crystalline and pore structure, the surface of activated carbon has a chemical structure. The adsorption properties are influenced by oxygen and hydrogen composition, and maybe a small amount of nitrogen. They may be associated with atoms of sulfur, nitrogen, and halogens. These heteroatoms become part of the chemical structure, or they become chemically bonded to the surface, rising to carbon-oxygen, carbon-hydrogen, and carbon-nitrogen compounds. [9] The presence of these heteroatoms compounds may influence the surface characteristics and properties of activated carbon.

Activated carbon is an amorphous sorbent and has high specific area (~1500m²/g). Activation (processing carbon to increase its surface area) can be accomplished by one of two methods: 1) physical activation, and 2) chemical activation.

1. Physical activation: The precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes:

   • Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600-900 °C, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)
   • Activation/Oxidation: Raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600-1200 °C.

2. Chemical activation: Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). Then, the raw material is carbonized at lower temperatures (450-900 °C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. This technique can be problematic in
some cases, because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material. [11]

The distribution of pore size determines the adsorption of large or small molecules. IUPAC suggested the classification: micropores (<2nm diameter), mesopores, (2-50nm diameter), and macropores (>50nm diameter). The major part of the internal surface area of activated carbon is generally contributed by micropores. Macropores and mesopores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics. Scanning Electronic Microscopy (SEM) is used to access the macropores. The pore size distribution is highly important for the practical application: In micropores, the molecule never escapes from the force field of the pore wall, even when in the center of the pore. Such pores mainly make a dominating contribution to the adsorption capacity for the molecules small enough to penetrate. The mesopores make some contribution to the adsorption capacity, but their main role is as conduits to provide access to the smaller micropores. Diffusion in the mesopores may occur. The macropores make very little contribution to the adsorption capacity, but they allow the adsorbate molecules to diffuse far with a minimum diffusion resistance. [12]

1.6 Activated Carbon Adsorption

In activated carbon adsorption, molecules from gas or liquid will be attached in a physical way to the surface. The adsorption process happens through three steps: 1) macro transport, which is the movement of organic material through the macro-pore system of the active carbon; 2) micro transport, which is the movement of organic material through the mesopore and micro-pore system of the active carbon; and 3) sorption, which is the physical attachment of organic material on the surface of active carbon in the mesopores and micropores of the active carbon. [11]

1.6.1 Elemental Mercury Adsorption
Elemental mercury is released into the environment predominantly by coal-burning power plants. The U.S. Environmental Protection Agency (EPA) estimates that 87% of the mercury entering the atmosphere in 1994 and 1995 was from combustion sources. Even though mercury is a trace element in coal with relatively low contents varying with coal rank, 0.01-3.3 mg/g, its emission into the environment can be harmful due to the large amount of coal burning [13].

Many existing air pollution control technologies have been used for the control of vapor-phase mercury emission from combustion process. Sodium sulfide (Na$_2$S) injection is used combined with dry sorbent injection (DSI) and fabric filters (FFs) for mercury capture. [14] Wet scrubbers are used to absorb mercury with gas-liquid contact. Activated carbon is employed in adsorption-based technology for mercury control.

Teller and Quimby researched the performance of activated carbon impregnated with copper chloride or sulfur for the removal of mercury. [15] They indicated that the moisture of the carrier gas and temperature had no effect on copper chloride impregnated carbon capacity for mercury. They also conclude that as the impregnate concentration of copper chloride increased, the capacity of mercury removal increased.

Shawn Manchester published a study that a set of carbon materials was treated by a choice of common oxidizers to investigate the mercury capture capacities at varying temperature conditions. [16] The combined results suggest that the ultra-high mercury capture efficiency is due to a subset of labile C–O functional groups with residual oxidizing power that are likely epoxides or (epoxide-containing) secondary ozonides. The results open the possibility for in situ ozonolysis to create high-performance carbon-based Hg sorbents. Also, the impregnated activated carbon was investigated for Hg capture. Impregnation optimized the existing properties of activated carbon giving a synergism between the chemicals and the carbon. The impregnation agent includes potassium iodide, sulfuric acid and sulfur. Matsumura [17] found that oxidized activated carbons adsorb 20-160 times more mercury than the untreated variety.

1.6.2 Sulfur Dioxide Adsorption
Sulfur dioxide emissions continue to have health and environmental effects. Flue gases from the combustion of coal generally contain <0.5% SO$_2$. The largest source of SO$_2$ is from stack gases from smelters handling sulfur ores, which may have up to 8% SO$_2$. Industrial processes such as wood pulping, paper manufacture and petroleum also form a major source of SO$_2$ from industry. Other sources of SO$_2$ include the emission from car exhaust and refuse incineration.

Many processes are employed for SO$_2$ removal from gas feedstocks, which can be categorized as absorption in liquid and sorption in solid. [18] Most commercial processes for SO$_2$ removal from gaseous emissions are for flue gas desulfurization (FGD). In FGD, SO$_2$ is removed predominantly by absorption and subsequent reaction with lime slurry. Other absorption processes include absorption in aqueous sodium carbonate or hydroxide or ammonia solution. Solid sorbents can also be used for the removal SO$_2$. There are several advantages of solid sorbents for SO$_2$ capture compared to liquid-based processes. The process will be less complex, so that it could be cheaper in construction, maintenance and operation. Regeneration of sorbent will be generally easier. Activated carbon and copper oxide process are widely used for SO$_2$ sometime cooperating NO$_x$ removal.

Activated carbon has been used for sulfur dioxide removal. The activated carbon catalyzes the oxidation of adsorbed sulfur dioxide in an oxygen atmosphere in relatively low temperature (below 180 °C). Water is required for the reaction to develop at a certain rate:

$$SO_2 + \frac{1}{2}O_2 + H_2O + \text{Activated Carbon} \rightarrow H_2SO_4$$

The adsorbent can be generated in one of the two ways: one is to wash with water to remove the sulfate as dilute sulfuric acid; the other is to heat the adsorbent to 420 °C to reduce the sulfate to sulfur dioxide. In the second way, the carbon performs as a reduce agent [19].

$$2H_2SO_4 + C \rightarrow 2SO_2 + 2H_2O + CO_2$$
When the gases do not contain any oxygen or water vapor, which is seldom the case, the SO\(_2\) adsorption takes place through adsorption. Alternatively, the adsorbed SO\(_2\) is oxidized to SO\(_3\) in the presence of oxygen, resulting in the formation of carbon-sulfur surface compounds. In activated carbon, the adsorption capacity is increased by a factor of the presence of air (oxygen) and the presence of water. Wu et al. showed the sulfur dioxide adsorption capacity by AC-carbon impregnated TEDA at the range of 195/5.5 (mg/g-C) to 235/6.5 (mg/g-C) with different TEDA concentrations. [20]

The reaction between calcium carbonate and sulfur dioxide takes place in pyrolyzed DPS adsorption. Calcium carbonate releases carbon dioxide on heating up to 840°C to form calcium oxide. The calcium oxide subsequently reacts with SO\(_2\)

\[
CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4
\]

\[
CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2
\]

1.6.3 VOCs Adsorption

Emissions of volatile organic compounds (VOCs) are generated from chemical process. They contribute to ozone formation in urban smog, and they can be toxic and cause odors. Many technologies have been investigated for VOCs emission control, such as catalytic oxidation, condensation, absorption, thermal incineration, bio-filtration, and membrane separation. Activated carbon is widely used as an adsorbent for organic gases and vapors, because of their developed surface and extended pore volumes.

Many researchers have investigated the adsorption of organic vapors on activated carbon. Li Yanxu published the experimental and theoretical studies made on the adsorption of toluene, ethyl acetate, benzene and their binary and ternary mixtures by activated semi-coke in an isothermal condition of 293 K. [21] C. L. Chang, etc investigated the adsorption of benzene and carbon tetrachloride onto activated carbon in mono- and binary-adsorbate systems. [22] The capacity of carbon to adsorb organic
compounds depends on the properties of the organics. In particular, large polar molecules tend to adsorb more strongly than small nonpolar molecules. Some common chlorinated solvents, such as vinyl chloride, are poorly adsorbed.

In chemical industry, activated carbon is used to capture organic vapors from non-condensable gas streams, such as process exhausts. For instance, the saturation vapor concentration of acetone in air at 20 °C is 340,000 ppmv. Cooling the process to -60 °C will leave about 1000 ppmv in the air. Carbon adsorption at 30 °C will reduce the outlets to below 100 ppmv. At the stream of 10,000ppmv, the adsorption capacities of three common industrial solvents - toluene, ethyl alcohol and acetone were reported: 40wt%, 33wt% and 29wt% at 75F, and Toluene 16wt% at 200F.[23]
Chapter 2

RESEARCH GOALS AND OBJECTIVES

Our hypothesis was that pyrolyzed DPS can be used as a sorbent to capture elemental mercury (Hg), sulfur dioxide, and organic vapors from gas streams.

The hypothesis was tested in this research by completing the following research objectives:

1) Assess the effects of pyrolysis temperature on the physical and chemical characteristics of the resulting sorbent materials.
2) Compare the adsorption capacities of the pyrolyzed DPS with those of BPL (Calgon Carbon, Pittsburgh, PA) and with those adsorbents in the literature for elemental Hg, SO₂, and VOCs. In this research, isoamyl acetate vapor was used as a representative VOC.
# Chapter 3

## EXPERIMENTAL APPROACH

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Description</th>
<th>Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Adsorbent preparation</td>
<td>Conduct pyrolyzed dry DPS at 900/750/600°C</td>
<td>Investigate temperature influence to the characters of pyrolyzed DPS</td>
</tr>
<tr>
<td>2. Adsorbent Characterization</td>
<td>X-Ray Diffraction (XRD)</td>
<td>Assess the bulk properties of the material</td>
</tr>
<tr>
<td></td>
<td>Scanning Electron Microscopy (SEM)</td>
<td>Assess the morphology of the material surface</td>
</tr>
<tr>
<td></td>
<td>Energy Dispersive spectrometry (EDS)</td>
<td>Assess the primary metal elements in the material</td>
</tr>
<tr>
<td></td>
<td>Fourier transform spectroscopy (FTIR)</td>
<td>Identify organic and inorganic compound</td>
</tr>
<tr>
<td></td>
<td>Brunauer Emmett Teller (BET)</td>
<td>Assess the surface area analyses of the materials</td>
</tr>
<tr>
<td></td>
<td>Thermo gravimetric Analyses (TGA)</td>
<td>Assess the mass change due to thermal degradation of the material</td>
</tr>
<tr>
<td>3. Measure the Adsorption Capacity of the pyrolyzed sludge for selected pollutants chemicals through breakthrough curves</td>
<td>Adsorption studies IAA by pyrolyzed DPS, BPL</td>
<td>Investigate absorption capability for organic compounds</td>
</tr>
<tr>
<td></td>
<td>Absorption studies with SO₂</td>
<td>Investigate absorption capability for reducible peroxide</td>
</tr>
<tr>
<td></td>
<td>Adsorption studies with Hg</td>
<td>Investigate absorption capability for heavy metals</td>
</tr>
<tr>
<td>4. Documentation and reporting</td>
<td>Documentation and reporting</td>
<td>Address the results, analysis and conclusion</td>
</tr>
</tbody>
</table>
Chapter 4

EXPERIMENTAL METHODS

4.1 Adsorbent Preparation

To prepare the carbon-based sorbents from DPS, 15g-20g dry DPS was inserted into a 10 mm diameter tube. Quartz wool was put to the two sides of the DPS to fix it at certain position. The DPS in the tube was then purged with nitrogen for 5 minutes to purge the tube of oxygen prior to pyrolysis. The tube was then loosely capped and put into a furnace. The furnace temperature was set to 600 °C, 750 °C, or 900 °C, and the DPS in the tube was heated for approximately 24 hours. Following pyrolysis, the sorbents were removed from the tube and stored in glass vials for subsequent characterization and evaluation. Figure 3 shows a schematic of the DPS in the tube as it was purged with nitrogen.

Figure 3. Schematic of DPS trapped between two plugs of quartz wool in tube.

Granular activated carbon, Calgon Carbon’s BPL (4X6, CALGON CARBON CORPORATION) was used as received.

4.2 Adsorbent Characterization
A sample of DPS from Appleton’s paper mill in West Carrollton, Ohio was characterized for its chemical and physical properties. Specifically, the ash content and metals content of the DPS were measured, and each is discussed in turn, below. Noted, however, is that the composition of DPS can change with time, even within the same mill, due to changes in the recycled fiber input to the pulping process. Therefore, the results presented here are representative of the DPS obtained from the West Carrollton mill at a selected time.

1. Ash content.

The ash content of DPS was calculated by comparing the mass of sample before and after heating it to 500 °C for 1 hour. In this study, the ash content of DPS was calculated to be 44%, which implies that 44% of DPS is inorganic and will not burn.

2. Metals analysis.

Table 2 compares the metals analysis of raw DPS from Appleton’s West Carrollton mill conducted in this study with those in a Canadian recycled fiber mill [24]. The values in Table 2 for Appleton’s DPS were obtained by extracting the metals from DPS samples with 100 mL 10% nitric acid and using inductively coupled plasma (ICP) to analyze the metals content in the extracts. Noted in Table 1 is that the predominant metals in DPS are calcium, iron, magnesium, and potassium. Sodium and sulphur are also present in relatively high concentration in our DPS samples, but concentrations for sodium and sulfur were not reported for the Canadian DPS sample. Notable differences between the two DPS samples are the copper and zinc concentrations, where our DPS sample has a much lower copper concentration (~20 % of the published DPS sample) and a much higher zinc concentration (>10 times that of the published DPS sample). Such differences are likely a result of the recycled fiber materials used in the paper mill process.

The data in Table 2 indicates that the raw DPS and the subsequent pyrolyzed DPS samples have significant concentrations of calcium in them. In addition, the presence of metals and their oxides likely affect their surface properties and porous structures, and
hence their adsorption performance.
Table 2 Comparison of metals content of DPS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Element</th>
<th>Appleton’s Mill in West Carrollton, Ohio 2007 (mg/kg)</th>
<th>Raw DPS Canadian Mill (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>1050±30</td>
<td>-</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>-</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>4.6± 3.5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.27±0.41</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>10600±4400</td>
<td>8300 ± 2300</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>-</td>
<td>4.7 ± 0.9</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>-</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>16±12</td>
<td>110 ± 19</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>606±15</td>
<td>430 ± 170</td>
</tr>
<tr>
<td>Lead</td>
<td>Ld</td>
<td>-</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li</td>
<td>1.1±0.8</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>1990± 72</td>
<td>620 ± 220</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25±1.1</td>
<td>20 ± 7</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>-</td>
<td>0.3 ± 0.3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>67±38</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>-</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>-</td>
<td>100 ± 7.4</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>170±13</td>
<td>154 ± 60</td>
</tr>
<tr>
<td>Selenium</td>
<td>Se</td>
<td>-</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>0.12±.12</td>
<td>-</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>900±36</td>
<td>-</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>68±2.5</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table 1: Averaged Elemental Concentrations of DPS

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>930±320</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>7.3±1.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>2.1±0.14</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>540±50</td>
</tr>
</tbody>
</table>

The pyrolyzed-DPS adsorbents were characterized by studying bulk properties, surface area, morphology and thermal degradation. The results of the characterization tests were used to assess differences in adsorption capacities for the sorbents synthesized in this research and for BPL activated carbon. The following techniques were used in the characterization of the pyrolyzed DPS and commercial BPL activated carbon.

- **X-Ray Diffraction**
- **BET surface area**
- **Scanning Electron Microscopy**
- **Energy Dispersive spectrometry**
- **Thermo gravimetric analyses**
- **FTIR analyses**

Each characterization method is discussed in turn below.

**4.2.1 X-Ray Diffraction**

X-Ray diffraction (XRD) studies were employed to investigate the crystal structure of the pyrolyzed DPS and commercial BPL, aimed to investigate the effects of pyrolysis temperatures.

XRD is widely used to characterize the bulk properties of the material. X-ray is electromagnetic radiation of wavelength about 1 Å (10-0.1 m). It occurs in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. X-ray primarily reacts with the electrons in atoms. Some of these photons from the incident beam will be deflected from their originally travel direction If the wave length of these scattered x-rays lose little energy, the process called elastic scattering, which we tend to measure in diffraction experiment. On the other hand, the electrons losing some of their energy will
have different wavelength than the incident x-rays. Diffraction of the X-rays through the sample provided some qualitative data about the presence or absence of graphite structures and the metal salt crystals in the products. The analysis of XRD relies on the application of Bragg’s Law.

\[ n\lambda = 2d \cdot \sin\theta \]

Where,
\( \theta \) = angle of incidence of X-ray beam, degrees
\( d \) = the distance between atomic layers in a crystal, Å
\( \lambda \) = the wavelength of the incident X-ray beam, Å
\( n \) = an integer

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms.

Diffraction patterns for the sorbents were recorded using a Scintag X-ray powder diffractometer with Cu K\( \alpha \) radiation source. Spectra were obtained from 4 to 60 degree at the step size of 0.04 and preset time of 0.5 second. Samples were measured in XRD at the voltage of 40kV and filament current of 35mA. The XRD equipment is connected to a computer with software used to record and analyze the diffraction data. The data is plotted by instrument response vs \( 2\theta \). For CaCO\(_3\), the predominant peak is at \( 2\theta = 29.7 \)°.

4.2.2 Brunauer Emett Teller

The adsorption of nitrogen at 77 K was used to assess the surface area of the materials according to Brunauer Emett Teller (BET) theory. A Beckman Coulter SA3100 BET was used to measure the surface areas of the sorbent with N\(_2\) adsorption. About 0.1 to 0.3g of the sample was out gassed at 120°C with a helium purge for 45 minutes prior to the surface area analyses. The concept of the theory is an extension of the Langmuir
theory, which is a theory for monolayer molecular adsorption. The resulting BET equation is expressed by:

\[
\frac{1}{\nu[(P_0 / P) - 1]} = \frac{c - 1}{\nu_m c} \left( \frac{P}{P_0} \right) + \frac{1}{\nu_m c}
\]

Where \(P_0\) = saturation pressure of adsorbate at 77K(atm)  
\(P\) = equilibrium pressure (atm)  
\(\nu\) = adsorbed gas quantity (cc/g) (STP)  
\(\nu_m\) = monolayer adsorbed gas quantity (cc)  
\(C\) is the constant related to the enthalpy of adsorption of the first layer, and it gives an idea about adsorbent-adsorbate interaction energies.

\[
c = \exp \left( \frac{E_1 - E_L}{RT_0} \right)
\]

Where \(E_1\) = heat of adsorption for the first layer (J/mol)  
\(E_L\) = heat of adsorption for the second higher layer (J/mol)  
\(R\) = gas constant (J/K-mol)  
\(T\) = temperature (K)

The BET method is used for the surface area calculation by physical adsorption of nitrogen molecules. A total area and a specific surface area are calculated by the following equations:

\[
S_{total} = \frac{\nu_m N_s}{RT}
\]

\[
S = \frac{S_{total}}{a}
\]

Where \(N\) = Avogadro’s number  
\(S\) = adsorption cross section (nm²)  
\(\nu_m\) = molar volume of adsorbate gas (cc)  
\(a\) = weight of sample (g)
4.2.3 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM, Zeiss Supra 35 VP FEG) was used to assess the morphology of the material surface. SEM is a type of electron microscope capable of producing high-resolution images of a sample surface, and shows the morphology of the sample.

4.2.4 Energy Dispersive Spectrometry

Energy Dispersive Spectrometry (EDS) was used to assess the primary metal elements in the materials. In SEM an electron beam is scanned across a sample's surface. The X-ray emitted has an energy characteristic of the parent element. EDS is used to detect and measure those energies, and thus can be used for elemental analysis. EDS can provide rapid qualitative, and with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1-2 microns.

EDS spectra were collected by using EDAX Genesis 2000. The sample preparation was same as that of SEM. The entire spectra were collected at an accelerating voltage of 20keV.

4.2.5 Thermogravimetric Analyses

Thermogravimetric Analyses (TGA, Perkin Elmer, Thermogravimetric Analyzer TGA 7) was used to assess the mass change, or thermal degradation, of the material as a function of temperature. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation. The analysis depends on a high degree of precision of three measurements: weight, temperature, and time. The experiments are usually run with a temperature ramp of 10 or 20 deg /min and can be carried out in an inert atmosphere, such as nitrogen, to study thermal stability or volatility.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture
content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

4.2.6 Fourier transform spectroscopy

Fourier transform spectroscopy (FTIR) is a measurement technique that was used to identify types of chemical bonds in a molecule by producing an infrared adsorption spectrum. FTIR is used to measure chemicals that are either organic or inorganic. It can be applied to the analysis of chemicals from spills, paints, polymers, coating, drugs, and contaminants. Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses. For FTIR, usually the tests in the concentration range of a few ppm up to the percent level.

The physical principles of FTIR are basic on molecular bonds vibrate at various frequencies, which depend on the elements and type of bonding. Each bonding, there are several frequencies it vibrating. The main component in the Fourier Transform Infrared (FTIR) spectrometer is an interferometer. It can splits and recombines a beam of light produces a pattern, which depends on wavelength. The Michelson interferometer is most commonly used. A Michelson interferometer consists of two mirrors and a beam splitter at the angle of 45 degrees to the mirrors. Germanium is usually coated on the beam splitter. When the light strikes the beam splitter, part of the light is transmitted through the beam splitter and half of it is reflected to the mirrors. Then the two mirrors reflect the light back and the light is combined at the beam splitter. Part of it can pass the sampling area and part is reflected to the source. The signal detector will detect the cosine wave.

Infrared spectra were collected with a Harrick Split pea ATR microscope interfaced to a Perkin Elmer 2000 Fourier transform infrared spectrometer. This accessory employed a silicon internal reflection element (IRE) and the standard deuterium triglycine sulfate (DTGS) detector on the Spectrum 2000 macro bench. Spectra collected using this device represent the average of 32 individual scans.
4.3 Adsorbent performance

4.3.1 Mercury adsorption test set-up

The experimental system, as shown in figure 4, includes a mercury permeation tube to generate elemental Hg vapor (METRONICS DYNACAL PERMEATION DEVICE, 10.0cm), a water bath, an adsorption cell, an online mercury analyzer (SHIMADZU, UV-1201S, UV-VIS Spectrophotometer) and a mercury absorption system.

The temperature of mercury vaporization was controlled at 55 °C by the water bath. Nitrogen was used as a carrier gas, and the flow rate was set at 1L/min. Mercury vapor mixed with nitrogen to generate an elemental Hg concentration of 10 ppbv. This gas stream was then passed through the sorbent bed, which was loaded in a glass adsorption tube with a filter. The sorbent to be tested (25mg) was mixed with 6g silica particles (Silica, S150-3 Fine Granules, Fisher Scientific). The silica provided a more porous fixed bed of adsorbent than would have been obtained with pure sorbent, thus reducing the pressure drop across the sorbent bed. The adsorption temperature was set at room temperature (20°C) and 140°C. An online mercury analyzer analyzed the Hg in the effluent from the adsorbent bed. A heater was located before the mercury analyzer in order to avoid condensation of mercury on the tubing. Following the Hg analyzer, the exhaust gas was scrubbed of Hg by a series of solutions before it was vented to a hood. The solutions used to absorb the Hg contained 4% (w/v) KMnO₄/ 10% (v/v) H₂SO₄. A pressure monitor was located at the end of adsorption system to test the pressure of the whole process. The soapy water was used in the pressure monitor to monitor the adsorption test was under atmospheric pressure.
4.3.2 Sulfur dioxide adsorption test set-up

A cylinder of 100 ppm sulfur dioxide in Nitrogen (Porta Cyl D model) was used for the adsorption experiments. As shown in Figure 5, the experimental set up consists of furnace, adsorption tube and sulfur dioxide monitor (TESTO Gas sensor, Model 350).

0.02 ml/min gas from the SO$_2$ cylinder was mixed with 1 L/min air prior to the adsorption tube, resulting in an SO$_2$ concentration of 20 ppm in air. The adsorption tube was glass, made with an inner diameter of 1cm. It was loaded with a mixture of 300 mg sorbent and 3 g silica. A filter was placed in the tube to hold the sorbent in place. The whole assembly was secured in a tube furnace. The tube furnace was used to control the adsorption temperature from room temperature to 100°C.
Figure 5 Schematic of the test system used for Sulfur Dioxide adsorption performance

4.3.3 Isoamyl Acetate adsorption test set-up

Isoamyl acetate (IAA, 98%, Sigma-Aldrich, 112674-100mL) vapor was generated using a diffusion cell, and the IAA vapor was mixed with nitrogen at $0.91 \times 10^{-3}$ mL/min. The nitrogen flow was 50 ml/min. The resulting IAA concentration in the gas stream was 18 ppm. The experimental apparatus is shown in Figure 6.

The gas flow was directed through the adsorption column, which consisted of 20 mg sorbent. The effluent from the adsorption tube was bubbled through 10 mL acetone for 15 minutes, which scrubs the IAA vapors from the nitrogen. The IAA-containing acetone solutions were then analyzed using a gas chromatograph (GC) (Hewlett Packard HP 6890) with a flame ionization detector. Chemstation software was used to obtain and analyze peak areas.

A calibration curve for IAA in acetone was obtained for the GC using solutions of known concentrations of IAA in acetone and graphing IAA peak area as a function of
IAA concentration. This calibration curve and the IAA peak areas from the GC for experimental samples were used to calculate the IAA concentrations in the experimental samples.

![Image of test system](image)

Figure 6 Schematic of the test system used for Isoamyl Acetate adsorption performance

The system calibration was conducted by peak areas from Gas Chromatography responding to certain concentrations of IAA in acetone. After components of the mixture (IAA and acetone) move through the GC column, they reach a detector. Ideally, components of the mixture will reach the detector at varying times due to differences in the partitioning between mobile and stationary phases. The detector sends a signal to the chart recorder which results in a peak on the chart. The area of the peak is proportional to the number of molecules generating the signal. The IAA peak appears at around 3.1 min; acetone peak appears at 1.7 min. As shown in table 3 and figure 7, the relation of IAA concentration in acetone and peak area on GC was calibrated.

<table>
<thead>
<tr>
<th>uL IAA / 10mL</th>
<th>Concentration (mg/L)</th>
<th>Peak Area at 3.1 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>0.5</td>
<td>43.55</td>
<td>5.1</td>
</tr>
<tr>
<td>1</td>
<td>87.1</td>
<td>11.9</td>
</tr>
<tr>
<td>5</td>
<td>435.5</td>
<td>62.3</td>
</tr>
</tbody>
</table>
Fig 7 IAA adsorption system calibration curve

y = 0.1661x
$R^2 = 0.9905$
Chapter 5

RESULTS AND DISCUSSION

5.1 Adsorbent Characterization

5.1.1 BET surface analysis

Table 4 shows the BET surface area and total pore volume of DPS pyrolyzed at 600 °C, 750 °C and 900 °C. Raw DPS and commercial BPL were also measured by BET for comparison.

Pyrolysis is an effective method that can significantly increase DPS surface area. BET surface area of the DPS increased by a factor of >10 following pyrolysis. The BET surface area of the DPS pyrolyzed at 900 °C was greater than that of the DPS pyrolyzed at 600 °C and 750 °C, likely due to the release of CO$_2$ upon decomposition of calcium carbonate in the DPS. This reaction expands the surface area due to the gas generation. Commercial BPL has the highest surface area (1100 m$^2$/g) of the samples used in this study by a factor of >10.

Table 4 BET surface area of adsorbents used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bet surface area (m$^2$/g)</th>
<th>Total Pore Volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw DPS</td>
<td>4.8</td>
<td>0.020</td>
</tr>
<tr>
<td>600 °C Pyrolyzed DPS</td>
<td>50</td>
<td>0.065</td>
</tr>
<tr>
<td>750 °C Pyrolyzed DPS</td>
<td>49</td>
<td>0.10</td>
</tr>
<tr>
<td>900 °C Pyrolyzed DPS</td>
<td>67</td>
<td>0.082</td>
</tr>
</tbody>
</table>
Figure 8 shows the pore size distributions of pyrolyzed DPS, Raw DPS and BPL. It appears that pyrolysis increased the sorbent pores volume compared to raw DPS. As the decomposition took place in DPS between 900°C and 750°C pyrolysis temperature. When the temperature increases, calcium carbonate was pressed, its bulk density was increasing. It may relate to the decreasing of volume from 750°C and 900°C pyrolyzed DPS. It is shown in Figmmmm, as the pyrolysis temperature increased from 600C to 900C, the percentage of the under 6nm diameter pores increased from 2.7% to 10.6%; the percentage of over 80nm diameter macropores increased from 30% to 75%. The dominating pore sizes in BPL are under 6nm diameter micropores and small mesopores; the over 80nm macropores in BPL is much less than those in pyrolyzed DPS. These differences affect the pressure drop according to pore sizes when vapor phase adsorption happens. Transport in a macropore can occur mainly by the bulk molecular diffusion. In very small pores in which the pore diameter is not much greater than the molecular diameter the diffusing molecule never escapes from the force field of the pore wall.
Figure 8 Pore size distributions of pyrolyzed DPS, BPL and Raw DPS

5.1.2 X-ray diffraction analysis

Figure 9 shows the XRD spectra of DPS pyrolyzed at 600 °C, 750 °C and 900 °C. Calcium carbonate is shown in the 600 °C and 750 °C samples. It is observed that the dominant crystal form is Calcite for all pyrolysis temperature samples. Calcite is the most thermodynamically stable among the three forms of CaCO₃, Calcite, Aragonite and Vaterite. [25]600°C and 750°C pyrolyzed DPS showed the same XRD pattern.

Calcium carbonate is the main compound found in 600°C and 750°C DPS. As the pyrolysis temperature increased to 900°C, carbon oxide becomes the main component due to the decomposition of carbon carbonate taking place between 750°C and 900°C. In the XRD spectra of the 900 C sample, CaO is identified by its peak at 32.34° 2θ and Ca(OH)₂ is identified by its peak at 34.11° 2θ. Part of CaO reacted with moisture in the air, thus Ca(OH)₂ was formed. Silicon dioxide is the only crystalline compound found in commercial BPL.
5.1.3 Scanning electron microscopy

Figure 10 shows the SEM photograph of DPS pyrolyzed at 600 °C, 750 °C and 900 °C and of BPL. The SEM allows visualization of the surface morphology of the samples. In SEM, the BPL sample appears to consist of layers of smooth flakes. Noted is that the fiber-shape carbon are present after pyrolysis. The fiber dimensions appear to be < 10um in diameter and up to 100 um in length. In BPL, the structure is different than that of the
DPS samples. Fig 11 shows the cellulose fiber remained in raw DPS. The rapid heating process remained the fiber shape through pyrolysis, which can explain 900°C sample kept the original fiber-shape carbon. However, in 750°C and 600°C samples, fibers collapsed when heating was relatively slow.

Figure 10 SEM images of Pyrolyzed DPS and BPL
5.1.4 Energy Dispersive Spectrometry Analysis

Table 5 shows the elemental composition of DPS after pyrolysis and of BPL. The samples are composed primarily of the elements carbon, oxygen and calcium. Hydrogen, too, is likely present, but EDS cannot detect it. In the DPS pyrolyzed at 600 °C and 750 °C, calcium and oxygen are mainly present as calcium carbonate, which is used as filler and in coatings in paper making processes. In the DPS pyrolysed at 900 °C, the carbon concentration decreases while the calcium concentration increases. This is likely due to the loss of carbon dioxide during the pyrolysis process as calcium carbonate decomposes to calcium oxide and carbon dioxide at temperatures between 800 °C and 900 °C. The main element in BPL is carbon. All DPS samples have comparable sulfur concentrations, whereas the sulfur content in BPL is approximately 4 times higher than that in the DPS samples.

Table 5 Table of Elementary Analysis of pyrolyzed DPS by Energy Dispersive Spectrometry Analysis

<table>
<thead>
<tr>
<th>At%</th>
<th>600 °C</th>
<th>750 °C</th>
<th>900 °C</th>
<th>BPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53</td>
<td>54</td>
<td>57</td>
<td>95</td>
</tr>
<tr>
<td>O</td>
<td>33</td>
<td>31</td>
<td>25</td>
<td>3.6</td>
</tr>
<tr>
<td>Mg</td>
<td>0.4</td>
<td>0.4</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>2.6</td>
<td>2.6</td>
<td>3.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Si</td>
<td>2.8</td>
<td>2.9</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>6.5</td>
<td>7.6</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ti</td>
<td>0.14</td>
<td>0.15</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

5.1.5 Thermogravimetric analysis

Figure 12 shows the TGA results of pyrolyzed samples and BPL under the nitrogen. As the samples heat to 900°C, it is noted that raw DPS has the highest weight change whereas the DPS pyrolyzed at 900 °C has the lowest weight change. This is as expected, since DPS undergoes significant decomposition and weight loss during the pyrolysis process. The remaining ash content can explain weight loss at around 600°C for pyrolyzed DPS after pyrolysis. The DPS pyrolyzed at 600 °C and 750 °C have a significant weight loss at approximately 840°C due to the decomposition of calcium carbonate. At 380 °C, raw DPS had a shape mass drop probably due to the ash and water left. At around 800°C, calcium carbonate decomposed, which happened the same as 750 °C and 600°C samples.
Figure 12 TGA curves of different temperature pyrolyzed DPS and BPL

5.1.6 Fourier transform spectroscopy

Figure 13 shows the FTIR spectra of pyrolyzed DPS and BPL activated carbon. Only CaCO$_3$ was found in all pyrolyzed DPS samples, and no organic components remained in the adsorbents. FTIR spectra of CO$_3^{2-}$ vibrational bands in calcium carbonate shows the peaks at 1470 cm$^{-1}$ and 870 cm$^{-1}$. [26] As pyrolysis temperature increased, the concentration of CaCO$_3$ dropped, which is noted by the decrease in signal. There is no organic or inorganic component found in the DPS or BPL activated carbon. [27]
Figure 13 FTIR curves of each type of pyrolyzed DPS and BPL

5.2 Adsorbent Performance

5.2.1 Adsorption for elemental Mercury

The adsorption capacity of pyrolyzed DPS and BPL were studied under room temperature (30°C) and high temperatures. 25 mg pyrolyzed DPS sample and 6 g silica solid were mixed as sorbent. The total flow including nitrogen gas carrying mercury vapor was 1 L/min. Controlled by the water bath, mercury flow was constantly 10 ppbv into nitrogen flow.

Figure 14 indicates the performance of 600°C, 750°C, 900°C pyrolyzed DPS and BPL for elemental mercury adsorption at room temperature (30 °C). In our study, the mercury adsorption capacity was tested as a function of pyrolysis temperature of DPS and adsorption temperature. 6 g silica only was used as control sample under the same condition. With only silica, mercury breaks through immediately (<20s). Figure 15 shows that DPS pyrolyzed at 750 °C and 900 °C has a much higher adsorption capacity for elemental Hg at room temperature than BPL carbon. However, the DPS pyrolyzed at 600 °C has comparable or slightly lower adsorption capacity for elemental Hg than BPL. This result may be due to the increase in pore volume as the pyrolysis temperature increased from 600 °C to 750 °C, and/or it could be due to subtle changes in surface structure. When the adsorption temperature was raised to 140 °C, the breakthrough of elemental Hg was within 1 minute for all samples.

The results showed significantly larger adsorption capacities at room temperature for DPS pyrolyzed at 750 °C and 900 °C than for DPS pyrolyzed at 600 °C and BPL. Noted from the BET analyses is that the pore volume increased and then decrease as pyrolysis temperature increased, especially at pore sizes > 20 nm. Therefore, possible reasons for the differences in adsorption capacities at room temperature for DPS pyrolyzed at 600 °C
compared to those for DPS pyrolyzed at 750 °C and 900 °C are differences in the pore volume within the samples. From BET analysis, the 600°C pyrolyzed DPS had the lowest pore volume and 750 °C DPS had the highest pore volume, which are consistent to the mercury adsorption. Compare to BPL, most pyrolyzed DPS performed higher mercury adsorption.

The adsorption of mercury on pyrolyzed BPL can be explained by the theory proposed by Dubinin [29] and Pierce, [28] the carbon surface contains some adsorption centers, called primary sites. When a molecule of the adsorbate adsorbs on a primary site, the adsorbed molecule can then act as a secondary center for the adsorption of more molecules. By combination of elementary analysis data, these primary sites may be those enriched with oxygen-containing functional groups, minor/trace elements such as sulfur and catalyzing components. However, the 600°C pyrolyzed DPS perform lower adsorption than BPL, the possible reason is that 600°C sample adsorption capacity was restrained by the lowest pore volume among BPL and pyrolyzed samples. Krishnan et al. [30] demonstrated that the virgin activated carbons adsorbed less mercury with increased temperature, and that heat pretreatment with clean nitrogen at 140 °C destroyed active sites, reducing the adsorptive capacity further still. Livengood et al. [31] showed that the adsorption capacity of sulfur impregnated carbon decreased with an increase in temperature from 55 °C to 90 °C.

Mercury adsorption capacities were calculated in Table 6. The calculation was expressed by ug Mercury/ g adsorbent. The mercury vapor density was conducted by Clapyron equation, 30°C: mercury gas density= 0.00806 g/cm³ and 140°C: mercury gas density= 0.00592 g/cm³. Adsorption capacity of silica only was 0. In coal burning combustion process, the amount of elemental mercury adsorbed by raw activated carbon is reported100ug/g, ZnCl₂ solution treated activated carbon enhanced its mercury adsorption capacity to 550 ug/g at 1% ZnCl₂ concentration solution and 900 ug/g at 5%.

Table 6 Mercury adsorption capacity (ug/g)
<table>
<thead>
<tr>
<th>Temperature</th>
<th>30°C adsorption</th>
<th>140°C adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600°C</td>
<td>750°C</td>
</tr>
<tr>
<td>Mercury adsorbed in 25 mg sample (ug)</td>
<td>0.40</td>
<td>3.3</td>
</tr>
<tr>
<td>Adsorption capacity (ug/g)</td>
<td>16</td>
<td>132</td>
</tr>
</tbody>
</table>

Figure 14 Affect of pyrolyzed temperature under 30°C for Hg adsorption
a) Affect of Hg adsorption temperature for 600°C pyrolyzed DPS

b) Affect of Hg adsorption temperature for 750°C pyrolyzed DPS

Figure 15 Affect of Hg adsorption temperature for pyrolyzed DPS

5.2.2 Adsorption for Sulfur Dioxide

The effects of pyrolysis temperature on sulfur dioxide breakthrough curves can be inferred from Figure 16, which presents the results obtained under 100 °C adsorption temperature for an SO₂ concentration of 20 ppm at 1 L/min. The results show that
pyrolyzed DPS has a higher adorption capacity for SO$_2$ than BPL, suggesting that adsorption is both physisorption and chemisorption in the DPS samples and only physisorption in BPL.

Figure 16 Affect of pyrolysis temperature in SO$_2$ adsorption

Figure 16 compares the adsorption of SO$_2$ at room temperature with that at 100 °C. Noted is that adsorption temperature has a much smaller effect on pyrolyzed DPS than it does on BPL.

a) 600°C Pyrolyzed DPS
b) 750°C Pyrolyzed DPS

c) 900°C Pyrolyzed DPS

d) BPL
Physical adsorption more likely happen under low temperature, while chemical adsorption overwhelms when adsorption temperature increased. Gas tends to be adsorbed on carbon solid at low temperature and van de Waals force is relatively strong at than case. On high temperature, sulfure dioxide is easily to be oxidized so the chemical adsorption happens.

Chemisorption of SO$_2$ on the pyrolyzed DPS likely occurs by the presence of CaCO$_3$ in DPS, and therefore, the adsorption capacity for SO$_2$ of the pyrolyzed DPS samples is greater than that of BPL. Conversion of CaCO$_3$ to CaSO$_4$ likely occurred within the adsorbent during the adsorption experiments. This is supported by the fact that adsorption temperature had a relatively small effect on adsorption capacity for the pyrolyzed DPS samples comapred to that for BPL. Contrastly, the adsorption capacity for BPL was largely affected by adsorption temperature, where lower adsorption temperatures resulted in higher adsorption capacities. This supports that adsorption on BPL was physical adsorption. Another possible reason that BPL has less adsorption capacity is that the pore size of BPL is dominated by mesopore and micropore. Because of capillary condensation, the equilibrium vapor pressure in a pore is reduced by the effect of surface tension. The small pores have less adsorption due to the vapor pressure in each pore. The pore size distribution is highly important for the practical application: In micropores, the SO$_2$ molecules are restraining in the center of the pores.

The effect of steam on SO$_2$ adsorption by pyrolyzed DPS and BPL is shown in Figure 18. Steam was introduced to the air stream by bubbling the air through a water-filled impinger. The results show obvious improvement in the adsorption capacity of the sorbents with steam than without steam. The adsorbed SO$_2$ is oxidized to SO$_3$ in the presence of oxygen, resulting in the formation of carbon-sulfur surface compounds. When the water vapor involved, the catalytic conversion to H$_2$SO$_4$ took place H$_2$SO$_4$ resolved in water and formed solution adsorbed by carbons and residued in adsorption char. The adsorption temperature increases, the catalytic activity was enhanced. As
showed in Figure 19, the higher temperature leads to a higher adsorption capacity when catalytic adsorption occurred.

a) 600°C pyrolyzed DPS

b) 900°C pyrolyzed DPS
c) 750°C pyrolyzed DPS

d) BPL

Figure 18 Affect of steam in SO₂ adsorption at 100°C

Table 7 SO₂ adsorption capacity (mg/g)
<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Empty</th>
<th>BPL</th>
<th>600°C</th>
<th>750°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>24.32</td>
<td>31.16</td>
<td>103.36</td>
<td>194.56</td>
<td>316.16</td>
<td>231.04</td>
</tr>
<tr>
<td>30°C</td>
<td>11.52</td>
<td>17.45</td>
<td>179</td>
<td>194</td>
<td>353.36</td>
<td>268.3</td>
</tr>
<tr>
<td>100°C with steam</td>
<td>9.54</td>
<td>10.61</td>
<td>185.88</td>
<td>259.41</td>
<td>437.04</td>
<td>298.11</td>
</tr>
</tbody>
</table>

Figure 19 Affect of temperature of steam in SO$_2$ adsorption

5.2.3 Adsorption for VOCs

The IAA adsorption by pyrolyzed DPS and BPL was conducted at room temperature. It is noted that the performance of pyrolyzed DPS increased slightly as the pyrolysis temperature increased. However, for all pyrolyzed DPS samples, the adsorption capacity of IAA was low, and the adsorption capacity of pyrolyzed DPS for IAA vapor at room temperature was much lower than that for BPL. The specific surface area is likely the critical parameter determining adsorption capacity for organic vapors. Pierce and Dubinin [31] observed that on an activated carbon surface, certain carbon-oxygen surface groups act as primary adsorption centers at which sorption of polar organic vapor
proceeds by way of hydrogen bonding. Higher surface area allows for more of these adsorption centers. However, when the samples were heated to 120°C after adsorption, the IAA was released. This suggests that the adsorption of IAA is dominated by physical adsorption. Therefore, BPL, with a surface area of approximately 20 times that of pyrolyzed DPS, has a much higher adsorption capacity for IAA vapor than pyrolyzed DPS.

Figure 20  The effect of pyrolysis for IAA adsorption

Table 8  IAA Adsorption capacity at room temperature (mg/g)

<table>
<thead>
<tr>
<th>No sorbent</th>
<th>900°C Pyrolyzed DPS</th>
<th>600°C Pyrolyzed DPS</th>
<th>BPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21</td>
<td>10</td>
<td>52.5</td>
</tr>
</tbody>
</table>
CONCLUSIONS AND RECOMMENDATIONS

De-inked paper sludge was pyrolyzed to synthesize adsorbents, which were characterized and evaluated for the adsorption of elemental Hg, SO$_2$, and isoamyl acetate vapor. The characteristics and adsorption performance of the pyrolyzed DPS samples was compared to those of BPL carbon. Key results that were obtained from this study are listed below:

- Pyrolysis increases the specific surface area of DPS, and solid sorbents were obtained with surface areas between 50 m$^2$/g and 70 m$^2$/g after pyrolysis at 600 °C, 750 °C, and 900 °C.
- After pyrolysis at temperatures up to 900°C, the presence of cellulose fibers was still observed in the samples.
- Between 750 °C and 900 °C, the calcium carbonate in the DPS was degraded to calcium oxide and carbon dioxide.
- Compared to commercial BPL, pyrolyzed DPS is dominated by pore sizes greater than 20 nm. Most pores sizes in BPL are less than 10 nm.
- The adsorption capacities of pyrolyzed DPS for elemental mercury are greater than those for BPL. The best adsorption capacity is 132 ug/g by 750 °C sample under 30 °C. Compare to former research, ZnCl$_2$ impregnated activated carbon performed 900ug/g adsorption at best. Most sulfur/metal impregnated activated performed better than pyrolyzed DPS.
- SO$_2$ adsorption of pyrolyzed DPS is also greater than those for BPL. Our best capacity is 437mg/g by 750°C at 100°C with steam. Wu showed best capacity for AC-carbon impregnated was TEDA 235/6.5 (mg/g-C), which is lower than pyrolyzed DPS.
- For all samples studied, steam enhanced the adsorption capacity for SO$_2$. 
• BPL had a much higher adsorption capacity for IAA vapor than pyrolyzed DPS. This is likely due to the much higher surface area of BPL compared to pyrolyzed DPS. Physisorption of IAA likely predominates on BPL and pyrolyzed DPS. No former research associated with IAA adsorption by activated carbon.
Future recommendations:

- In the present research, the samples were not activated by steam or chemical addition. Rather, it was assumed that the DPS samples were activated by the presence of metal oxides and salts already contained in the DPS. It is recommended that DPS be mixed with a chemical activation compound to enhance its surface area and active surface sites.
- In this study, adsorption isotherms were not obtained in the lab. It is recommended that adsorption isotherms for elemental Hg and SO$_2$ be obtained experimentally for pyrolyzed DPS.
- The mechanism of adsorption could be investigated for Hg and SO$_2$. Analyses of the surface of pyrolyzed DPS before and after adsorption may provide evidence of adsorption mechanisms for elemental Hg and SO$_2$.
- The use of pyrolyzed DPS as a catalyst for Hg oxidation and/or VOC oxidation would be of interest. The metals contained in DPS could be used as active sites in catalytic oxidation processes.
REFERENCE


13. Hsi H; Chen S; Rostam-Abadi M; Rood MJ, Richardson CF; Carey TR and Chang R. *Energy Fuels* 1998, 12, 1061.


