PROJECT REPORT
MIT-6

Color and Chlorinated Organic Reduction in Kraft Pulp Mill Wastewater using Activated Petroleum Coke

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ISBN 1-55261-012-8

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Report Number MIT-~~1~~16
Minimal Impact Technologies Theme
Sustainable Forest Management Network of Centres of Excellence
Life Cycle Impacts of Wood Fiber Processing

January 1999

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ACKNOWLEDGEMENTS

This project was funded in part by the Sustainable Forest Management Network of Centers of Excellence and part by a research grant to Dr. D.W. Smith from the Natural Sciences and Engineering Research Council of Canada. In addition, a controlled atmosphere furnace was made available by the Western Research Center (CANMET) as was one from the School of Mining and Petroleum of the Department of Civil and Environmental Engineering.

The initial phase of the work was pursued by a graduate student, terminated, and started with a new experimental design and equipment. This report is the result of the work since the restart.

The authors would like to acknowledge Suncor Canada for providing the petroleum coke samples and Weyerhaeuser Canada for providing the bleached stage wastewater samples used in this study. Also, the authors would like to thank Ms. Maria Demeter for performing the chemical analyses used in this study. The efforts and assistance of Ms. Nola Low in editing and formatting this document are also acknowledged with great appreciation.

EXECUTIVE SUMMARY

The main objective of this study is to use an abundant waste by-product from the oil sand industry in the production of activated coke. The activated petroleum coke will be evaluated for use in the removal of color and chlorinated organic compounds from Do bleaching stage wastewater. Utilization of the petroleum coke provides an excellent disposal option for the oil sand industry and provides a cheap source of activated coke. Also, the spent activated coke can be utilized as a fuel source for generating steam and electricity.

In this study, activation of petroleum coke was evaluated using a fixed-bed two-step carbonization/activation process at a temperature of 850°C with steam as the activation medium. Preliminary results, in terms of methylene blue adsorption, indicated that the activation process was successful. The methylene blue adsorption results showed that higher amounts of methylene blue were adsorbed per 100 grams of activated coke compared with raw petroleum coke.

High color and AOX reduction were achieved using activated coke, and were confirmed by the adsorption equilibrium experiments. Using an activated coke dose of 15,000 mg/L resulted in about a 90% reduction in color and a 87% reduction in AOX. Previous studies on the adsorption of nonbiodegradable matter in biotreated wastewater using different types of activated carbons showed that more than 90% reduction in color and AOX was achieved when an activated carbon dose in excess of 10,000 mg/L was used (Çeçen, 1993). The adsorption results also showed that increasing the activation time from two to four hours increases color and AOX reduction.

The activated coke dosage required for high color reduction in the bleached kraft mill wastewater is considered high, leading to cost concerns. However, the amount of color adsorbed per gram of activated coke is relatively high, ranging from 140 to180 mg/g. Also, the high cost associated with using activated coke could be offset by using an abundant source of petroleum coke, currently stockpiled in large quantities, so that costs are associated only with the activation process.

Based on the encouraging results of this study, further research on using activated coke for color and chlorinated organics is required. Recommended future research includes:

1. Optimization of the activation of petroleum coke for color and AOX reduction. This can be achieved by activating the coke at different steam-to-carbon ratios as well as for longer periods.
2. Adsorption kinetic studies are required to determine the time required for certain removal efficiencies of color and AOX. This information would aid in sizing the reactor used for mixing or contacting the activated coke and bleached kraft mill wastewater.
3. Evaluation of different methods to separate the spent activated coke from the wastewater, e.g., dissolved air flotation.
4. Evaluation of different methods to utilize the spent activated coke, e.g., in direct combustion for steam generation

1. INTRODUCTION

Bleached kraft pulp mill wastewater is the most problematic part of the whole pulp industry. These effluents contain high concentrations of color-causing compounds, mainly due to lignin. Also, high concentrations of chlorinated organic compounds are present due to the bleaching of pulp with chlorine and chlorine dioxide. Discharge of these deleterious compounds into a receiving water body can impact the ecological balance and causes esthetic concerns. In addition, chlorinated organic compounds may be associated with some toxicity and show considerable resistance to biological and chemical degradation. Therefore, kraft mills are required to reduce color-causing and chlorinated organic compound concentrations before discharging effluent to a receiving water body.

Almost all Canadian pulp mills use some sort of biological treatment system to reduce BOD and TSS concentrations in their effluent. However, available evidence indicates that biological treatment is not very effective in reducing color and chlorinated organics in pulp mill wastewaters (Çeçen et al., 1992).

There are other effective treatment alternatives for color reduction in bleached kraft mill effluent. Activated carbon adsorption is considered very effective in the reduction of color and in the removal of the nonbiodegredable fraction of pulp bleaching effluent. However, the production of activated carbon is costly.

One option for substantially reducing the high cost of using activated carbon adsorption is by producing activated carbon from an abundant and cheap source of raw carbonaceous materials. A potentially abundant and cheap source is petroleum coke, which is a by-product of the upgrading of bitumen from oil sands into synthetic crude oil. There are two existing oil sand plants in Northern Alberta, which produce about 3000 tonnes of petroleum coke per day. Syncrude Canada Ltd. produces fluid petroleum coke, which is presently discarded, and Suncor Inc. produces delayed petroleum coke of which 10 to 20% is used as fuel with the rest stockpiled.

This waste petroleum coke could be utilized as a cheap and readily available raw material for the production of valuable activated carbon suitable for the removal of color from bleached kraft pulp mill wastewaters. Previous studies on the activation of fluid coke, using a simple two-step carbonization/activation procedure, showed that activated coke has an adsorptive capacity 20 to 50 times greater than raw fluid coke (Di Panfilo, 1995), and roughly one quarter that of commercial grade activated carbon. The activated coke produced has the ability to adsorb large organic molecules such as methylene blue dye. The adsorptive capacity is attributed to the large surface area and porosity created during activation. The maximum N_2 BET surface area developed was 318 m^2/g at a porosity of 240 mm^3/g, which was produced by steam activation of raw coke at a temperature of 850°C with a soak time of six hours.

This study seeks to utilize an abundant waste by-product from the oil sands industry in the production of a valuable activated carbon. The activated petroleum coke will be used in the removal of color and chlorinated organic compounds from bleached kraft pulp mill wastewaters. The utilization of petroleum coke provides an excellent disposal option for the oil sands industry. Also, the spent activated coke can be used as a fuel source for generating steam and electricity. This is depicted in the schematic diagram shown in Figure 1.

The primary objectives for this stage of the study are:

1. to evaluate the production of powdered activated carbon from petroleum coke using a fixed-bed two-step carbonization/activa-

tion procedure, where steam will be used as an activation media, in terms of methylene blue adsorption; and

2. to evaluate the powdered activated petroleum coke, using adsorption isotherms, for color reduction (measured at 465 nm), UV absorption reduction (measured at 254 nm) and AOX reduction, on D_o bleaching stage wastewater.

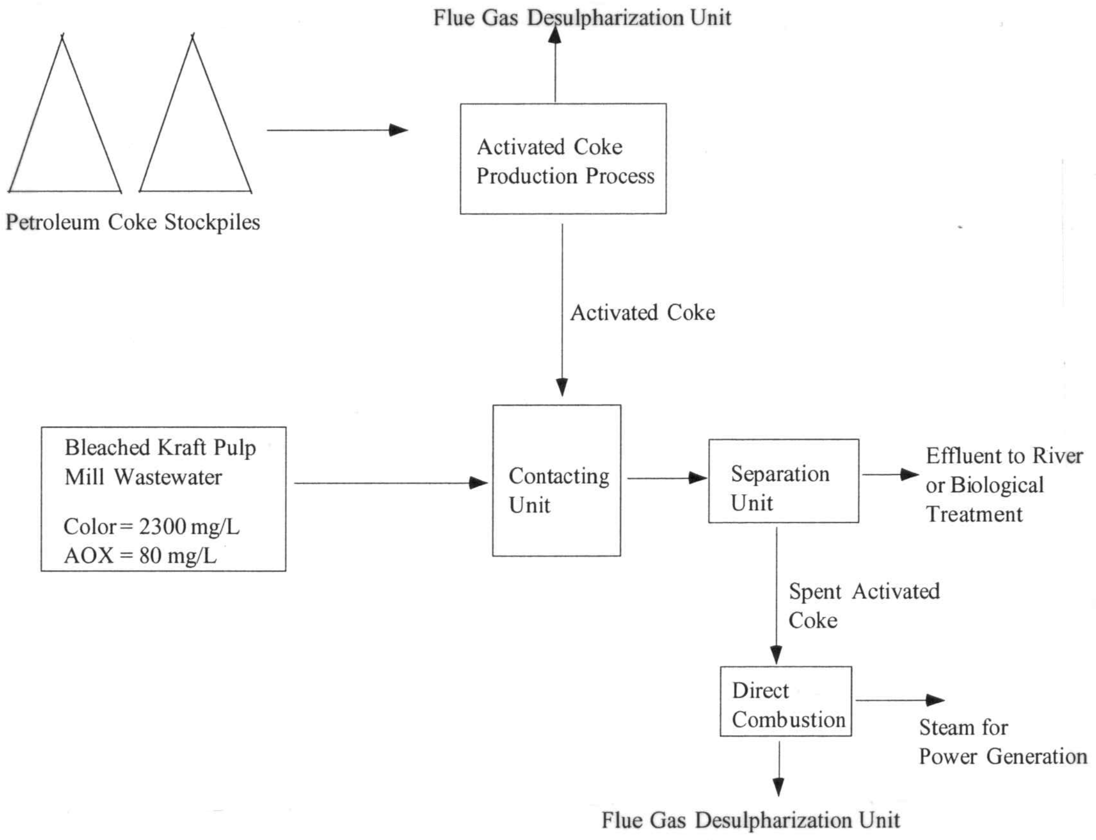

Figure 1. Schematic diagram for utilizing petroleum coke to reduce color and chlorinated organics in bleached kraft mill wastewater.

2. LITERATURE REVIEW

Bleached Kraft Pulp Mill Wastewater

The pulp and paper industry is one of the largest industrial consumers of water worldwide. As a result, trillions of tonnes of wastewater carrying more than 2.5 x 10^6 tonnes of derivatives including about 250,000 tons of chlorinated organics were discharged annually by the industry in 1980 (Kringstad and Lindström, 1984). The released effluent has major environmental impacts on the aquatic environment, such as:

1. discolorization of the receiving water and reduction of photosynthesis activities;
2. deteriorating the biological and chemical quality of water;
3. acute and chronic toxicity;
4. taste and odor;
5. slime growth; and
6. surface water foaming.

The pollution parameters associated with color-causing substances and chlorinated and non-chlorinated toxic organic matter are classified as nonconventional pollutants (USEPA, 1990; Environment Canada, 1983). These pollutants create the biggest problems for the pulp and paper industry and the regulatory authorities.

Bleached kraft pulp mill wastewater characteristics

Color. The color in pulp mill effluent results mainly from the operations of pulping and bleaching. In a representative bleached kraft mill 135 kg of color per tonne is generated. The dominant color stream in the bleach plant is the caustic extraction process. Even though there are no well-established color discharge regulations and there is little scientific data on color associated problems, the pulp industry has attempted to address the color problem for many years.

The major components of the color body in pulp mills are lignin and lignin derivatives (Çeçen, 1993). In bleached kraft pulp mill effluents most of the lignins are chlorolignins (Jokela et al., 1993). This results from the addition of HCl and nucleophilic substitutions with chlorine-containing compounds during prebleaching or final bleaching (Kringstad and Lindström, 1984).

The organic compounds contained in bleached kraft pulp mill effluents not only vary by chemical type but also are widely distributed from low to very high molecular weight (MW) (Crooks and Sikes, 1991). Work with biotreated plant effluent has attributed most of the color, measured by absorption at 436 nm, to chlorolignins that have a molecular weight ranging from 100 to 10000 (g/mole) (Yin et al., 1990).

Chlorinated organics. Chlorinated organic substances are organic compounds that have one or more chlorine atoms attached to the molecule. In bleached kraft mills, these chemicals are found in the effluent as chlorinated phenols, chlorinated acids, alcohols, aldehydes, ketons, sugars and aliphatic and aromatic hydrocarbons.

It has been reported that the low MW (<1000 g/mole) organic bond chlorine (O-Cl) forms 30% of the O-Cl in spent chlorination liquor and 5% of O-Cl in the caustic extraction liquor (Kringstad and Lindstöm, 1984). Although this fraction is low, it has profound adverse effects on the aquatic ecosystem due to the potential acute toxicity of some of the compounds.

Almost 80% of the chlorinated organic compounds in bleached kraft mill effluent derived from lignin derivatives are of high molecular weight (MW>1000 g/mole) (Kringstad and

Lindstöm, 1984). Only 10 to 40% of the chlorinated organic compounds have been characterized, therefore it is impractical to characterize effluents on the basis of individual substances. A surrogate measure for total organochlorine concentration in effluent is thus required.

A commonly used surrogate measure for organochlorine concentration in effluents is absorbable organic halide (AOX). AOX measures volatile halides that are associated with organic compounds, which are adsorbed onto granular activated carbon at a pH of 2 (Gergov et al., 1988).

Strategies for removal of color and chlorinated organics

There are two general strategies for the reduction of color and chlorinated organics from pulp mill effluents. The first strategy attempts to modify the manufacturing process so that less color and toxicants are produced or released. For example, recent developments in process technology such as oxygen/ozone bleaching, have greatly reduced the effluent volume and load in the bleaching plant. However, implementation of these technologies is currently expensive. In addition, process modifications may not be technically feasible in all mills because of the lack of flexibility within the mill or incompatibility between the proposed process modifications and the desired end products.

The second strategy includes the use of physical, chemical and biological processes such as ultrafiltration, activated carbon adsorption, ozonation and activated sludge. The most common process used is the conventional biological treatment, which effectively reduces BOD, TSS and the concentration of individual resin and fatty acids in kraft mill effluents. However, biological processes are not effective in the removal of color-causing molecules (Çeçen et al., 1992) and chlorinated resin acids (Chung et al., 1979), which are considered non-biodegradable or recalcitrant.

Activated carbon adsorption is very effective in the reduction of color and the removal of the nonbiodegredable fraction of pulp bleaching effluent (Çeçen et al., 1992). However, this process has high costs associated with the production of activated carbon and the disposal and/or regeneration of spent activated carbon. An estimated total cost of $10/tonne is required for an 80% reduction incolor for combined mill effluent (Springer, 1985).

Using activated carbon produced from an abundant and cheap source of raw carbon material could substantially reduce the high cost of activated carbon production, and eventually the operation cost. A potential abundant and cheap source is petroleum coke, which is a by-product of the upgrading of bitumen from oil sands into synthetic crude oil.

The following section will discuss the use of petroleum coke as a raw carbon source, the physical and chemical characteristics of activated carbon, the production of activated carbon and the adsorption of BKME effluent with activated carbon.

Activated Carbon

Activated carbon is a predominantly carbon compound with the ability to adsorb molecules from an aqueous or gaseous stream. It is manufactured from carbonaceous material to produce a high carbon content, highly porous and large internal surface area with very good, universal adsorptive properties. It is prepared from various high carbon content raw materials such as coal, petroleum coke, wood, almond shells and coconut shells. The raw material used has a profound impact on the physical and chemical properties of the activated carbon produced (Sontheimer et al., 1988).

Petroleum coke as a raw carbon source

Two types of petroleum coke are of potential interest for this study. Both are derived from the Athabasca oil sands bitumen upgrading operations in northern Alberta, Canada. Suncor Canada produces about 300,000 tonnes per day of delayed petroleum coke while Syncrude Canada produces about 200,000 tonnes per day of fluid petroleum coke.

Delayed petroleum coke. Delayed petroleum coke is produced in a coking drum heated to 480°C. Volatile material is removed and the remaining by-product is broken up hydraulically and then removed from the drum. The delayed coker particles are irregularly shaped and display no visible porosity down to 500 microns. The particles range in size from a few microns to a few tens of millimeters (Jack et al., 1979).

The coke has an amorphous (noncrystalline) structure, where 92% of the carbon atoms are aromatic (Majid et al., 1989). The reactivity of delayed petroleum coke, in terms of oxidation, is extremely low (Watkinson et al., 1989). The proximate analysis, ultimate analysis and heating value of this coke are given in Table 1 (Watkinson et al., 1989). The ash content of Suncor coke (in terms of w/w%) is summarized in Table 2. It shows that the coke has a high ash content containing high concentrations of vanadium, nickel and iron (Majid et al., 1989).

The activation of delayed petroleum coke has been attempted by different researchers (Tollefson, 1978). A specific surface area in the range of 220 to 400 m^2/g was generated.

Fluid petroleum coke. Fluid petroleum coke is produced in a fluidized bed reactor at 600°C to 1000°C (Bryers, 1993). A thin film of bitumen is sprayed onto a fluidized bed consisting of hot coke particles. The volatile material is driven off to be upgraded into synthetic crude oil and the coke particles get coated with a layer of coke. Excess fluid coke is removed from the reactor to be discarded.

Table 1. Properties of delayed and fluid petroleum coke (Watkinson et al., 1989)

	Coke Type	
	Delayed Coke	**Fluid Coke**
Parameters ↓	**Proximate Analysis (Wt % as received)**	
Ash	3.0	8.0
Volatile	11.9	6.9
Moisture	1.8	3.7
Fixed carbon	83.3	81.4
Parameters ↓	**Ultimate Analysis (Wt % dry)**	
C	84.9	79.5
H	3.9	1.6
N	1.3	1.7
S	6.0	7.0
Cl	0.0	0.7
O	0.8	1.2
Heating Value (dry, MJ/kg)	34.7	29.7

Table 2. Coke ash content in w/w% (Majid et al., 1989).

Parameter ↓	Coke Type	
	Delayed Coke	Fluid Coke
SiO_2	41.7	40.6
Al_2O_3	19.2	21.5
Fe	16	8.4
Ti	1.5	2.0
Ni	1.6	0.7
V	2.8	1.8

The coke consists of solid, spherical particles ranging in size from a few microns to 20 mm. The spherical particles have an "onion skin" internal structure consisting of 30 to 100 layers of coke (Di Panfilo, 1995). The high temperature conditions produce non-porous graphitized carbon as indicated by its low amenability to acid leaching (Jack et al., 1979). All the carbons are aromatic and about 45% of the carbons are bonded to hydrogen atoms (Majid et al., 1989).

The proximate analysis, ultimate analysis and heating values for fluid coke are given in Table1 (Watkinson et al., 1989). As shown in Table 1, the fluid coke has a higher sulfur content (7.0%) than the delayed coke (6.0%). Also, the fluid coke has a lower heating value (29.7 MJ/kg) than the delayed coke (34.7 MJ/kg). The ash content of fluid coke (in terms of w/w%) is shown in Table 2. This table shows that fluid coke has a lower ash content in terms of concentrations of vanadium, nickel and iron compared to the delayed coke.

Different researchers have attempted the activation of fluid petroleum coke. Metrailer (1974) activated fluid coke by heating at 425°C for 11 hours to 35% burn-off. Steam was added at a rate of 0.25 m^3/h per pound of coke at 900°C for six hours to achieve a total burn-off of 70%. DiPanfilo (1995) activated fluid coke at 850°C for six hours using steam. The activated coke had a BET surface area of 318 m^2/g and a porosity of 2.4×10^{-4} m^3/kg.

Physical and chemical characteristics of activated carbon

Activated carbons are characterized by a very large specific area with typical values ranging from 100 to 1000 m^2/g and a large specific pore volume ranging from 2×10^{-4} to 1×10^{-3} m^3/kg (Jankowska et al., 1991). Its high adsorptive capacity is derived from its maze of interconnected pores with their associated surfaces. The pores are classified according to diameter based on the observation that many pores are cylindrical in shape. The internal structure is composed of different sizes of pores known as micropore, mesopore and macropore.

Micropores have diameters of less than 20 nm, which make up 20 to 40% of the total pore volume but up to 95% of the total surface area. Therefore, the micropores are where most adsorption occurs. The adsorption mechanism is volume filling where the adsorbate and the pore have similar dimensions.

Mesopores range in size from 20 to 500 nm diameter. The total volume of mesopores varies from 20 to 35% and the surface area ranges from 5 to 25%. The mesopores provide a route for the adsorbate to migrate to an adsorption site. The adsorption mechanism in the mesopores is by capillary condensation, which occurs by the laying down of multiple layers of adsorbate followed by volume filling.

Macropores are the third size category and have diameters greater than 500 nm. The surface areas of macropores is often less than 5% of the total surface area and constitute up to 30 to 50 % of the total pore volume. Macropores are not important for providing adsorption sites. However, they act as transport arteries for the adsorbates to migrate from the exterior fluid medium to the interior of the carbon particle.

The pore size distribution in activated carbon determines the amounts of various types of adsorbates that can be adsorbed (Sontheimer et al., 1988). An activated carbon that is has optimal surface area for one adsorbate may be a poor adsorbent for another. Therefore, it is important in this study to optimize the pore size distribution of the activated petroleum coke for the adsorption of the color-causing compounds present in the bleached kraft mill wastewater.

Activated carbon surface chemistry has an important effect on the types of molecules that can be adsorbed. Activated carbon consists of 5 to 20% elements other than carbon. These elements include oxygen, hydrogen, sulfur, nitrogen, halogens and metals. Oxygen is the most important element in determining the polarity characteristics of the activated carbon, which has a bearing on the type of molecules that can be adsorbed. Various types of functional groups such as carboxylic, hydroxyl and carbonyl are present on the surfaces of activated carbon, which can increase the polarity of the surface (Sontheimer et al., 1988). This could increase the adsorption of more polar compounds and decrease the adsorption of less polar compounds. If the activated carbon surface was too polar, then water would significantly compete for adsorption sites with the target compounds.

Activated carbon can contain acidic or basic groups depending on the activation temperature that was used for its production. If the activation temperature was above 500 to 600°C, then the attached groups are primarily basic. At lower activation temperatures the attached groups are primarily acidic. Activated carbon with basic groups should be used for the adsorption of acidic compounds, such as oxidized lignin.

Production of activated carbon

The overall manufacture of activated carbon from a raw carbonaceous material involves two main stages: carbonization and activation. Carbonization increases the carbon content of the raw material by pyrolysis. In this process, the carbonaceous material is heated in an inert atmosphere to drive off moisture and volatile matter. Selective treatment with activating gases such as steam then forms the actual pores, fissures and cracks and is termed activation. In this process high temperatures, in the range of 800 to 1000°C, are required in order to achieve a high enough reaction rate.

Carbonization stage. The initial porous structure of activated carbon is first developed during the carbonization stage. In this stage, also known as pyrolysis, the proportion of carbon in the raw carbonaceous material is increased by reducing the water content and the volatile matter. This process is carried out in stationary, rotary or fluidized bed ovens.

The parameters that affect the properties of the carbonaceous material are the maximum temperature of heating, time of heating and the carbonization atmosphere. The maximum temperature of heating is the most important parameter and most carbonization occurs at temperatures of 500 to 800°C. Higher temperatures would crystallize the carbon into graphite, which is very difficult to activate.

Initially, the high temperatures of carbonization release moisture and volatile matter from the interior of the particle resulting in a branched system of pores. Thermal decomposition of organic matter also produces gases, which escape the particle. The remaining material consists of macromolecules mainly composed of carbon. This carbon begins to condense and polymerize forming sheets of aromatic carbons. These sheets of aromatic carbons tend to combine forming microcrystals similar to graphite.

The spaces between the microcrystals form the primary porosity of the carbon. These pores are usually filled with tar and amorphous carbon from thermal decomposition of the organic matter. The presence of these initial micropores influences the rate of activation to follow. These pores facilitate the diffusion of activating gases into the carbon particle by increasing the surface area for activation, therefore increasing the overall activation rate.

Thermal decomposition during carbonization leads to the formation of gases and vapors, especially CO_2 and water vapor. These can react chemically with the carbon structure unless they are quickly removed with a fast flow of inert gas such as nitrogen.

Activation stage. The activation stage is the most important process in the manufacturing of activated carbon, where porosity, high surface area and surface functional groups are produced. In this process, the carbonized material is treated with an activating gas, such as steam or oxygen, at high temperature. The oxidizing gases react first with tar and amorphous carbon deposits inside the initial pore structure, or the microcrystals, of the carbonized material. These gases oxidize the carbon to form carbon oxide gases, which are released to the atmosphere. Next, the oxidizing gases react with the carbon on the pore wall, which make up 14% of all the carbons in the microcrystals. The oxidation proceeds along the pores widening them as it progresses.

Activation is often a non-homogeneous process where irregular pits and channels are formed. The process is carried out until the maximum surface area is achieved. The maximum surface area usually occurs when 50% of the carbon structure has been burned off (Jankowska et at., 1991). Beyond this point of activation, further oxidation starts to burn through the walls of the pores decreasing the total surface area.

The most important variable in the activation process is temperature. At too low an activation temperature, only the most reactive carbons are oxidized and the microcrystals may not be oxidized at all. At too high an activation temperature, all the carbons react with the oxidizing agents and thus the first carbons to react are on the exterior of the carbon particle. As a result, porosity is not developed and the carbon particle is quickly consumed.

Removal of color and chlorinated organics by activated carbon adsorption

Work on the removal of color and chlorinated organics from bleached pulp mill effluent using activated carbon adsorption was performed by Çeçen (1993). In this study, spent bleaching effluents from the chlorination and extraction steps of a sulfate pulp mill were subjected to activated carbon treatment to investigate the removal of color and chlorinated organics. This effluent was treated with different types of commercial activated carbons.

Generating adsorption isotherms for the parameters COD, DOC, color (measured at 436 nm) and UV absorption (measured at 254 nm) determined the degree of color and chlorinated organics removal. The removal level for color and UV adsorping materials was over 90% when the carbon dosage exceeded 10,000 mg/L. In addition, more than 90% of AOX was removed.

In this study, there was a slight increase in the adsorptive capacity of the activated carbon when the initial pH of the wastewater was decreased to 5.2. In particular, color reduction was remarkably higher than the other parameters, i.e., COD, DOC and UV_{254}, at lower pH values. This indicates the preferential removal of high molecular weight chlorolignins (Ying and Tucker, 1990).

In addition, the study showed that better adsorptivity was obtained when the adsorption was expressed in terms of UV_{254} and $color_{436}$ rather than the DOC parameter. It was reported that the UV analysis would reflect the removal of haloginated organics better than DOC (Sontheimer et al., 1988). Therefore, rapid UV_{254} analysis and $color_{436}$ measurement could be used to investigate the adsorption of AOX compounds and high molecular weight chlorolignins, respectively, from bleached kraft mill wastewater.

Potential Problems Associated with the Production of Activated Coke and the Disposal of Spent Activated Coke

One of the potential environmental problems associated with the production of activated petroleum coke is sulfur emissions. During the activation of coke large amounts of H_2S and SO_2 will be released (Watkinson et al., 1989). One of several options to eliminate these emissions is to use the flue gas desulpharization process. Therefore, a practical solution to these emissions would be locating the petroleum coke activation process at a site close to sulphur removal facilities. Suncor, Canada, has such a facility, which is used to reduce emissions released as a result of coke combustion (used for steam and electricity generation).

Dioxin production, as a result of the thermal combustion of the spent activated coke that was used for the adsorption of chlorolignins, is another potential environmental problem. However, production of dioxins could be eliminated if thermal combustion of the petroleum coke is performed at 700 to 1000°C (Choudhry et al., 1980; Naikwadi, 1995).

The land application of ashes, which are produced as a result of the thermal combustion of spent activated coke, could cause leaching of metals into the soil and underground water. Nickel is one of the metals found in high concentrations in petroleum coke. This metal could cause some phytotoxicity if it accumulates in plant tissues (Environment Canada, 1983). To avoid this potential problem, the ash should be disposed of into properly designed landfills.

3. EXPERIMENTAL METHOD

The experimental method for this stage of the study is divided into two parts. The first part involves the production of activated carbon from petroleum coke using a fixed-bed two-step carbonization/activation procedure, where steam is used as an activation medium, and the product is evaluated in terms of iodine and methylene blue numbers. The second part involves the evaluation of activated petroleum coke for the removal of color and chlorinated organics from D_0 bleaching stage wastewater. This is achieved by performing adsorption isotherms, where color (measured at 465 nm), UV absorption (measured at 254 nm) and AOX of the wastewater are measured at different carbon dosages after reaching equilibrium.

Experimental Procedures for the Production of Activated Coke

Preparation of raw petroleum coke

In this study, delayed coke from Suncor was used as the source of raw petroleum coke for the following reasons:

1. The volatile content of the delayed coke (11.9%) is higher than that of the fluid coke (6.9%). This allows for better development of initial pore structure in the delayed coke during the carbonization stage.
2. The sulfur content of the delayed coke (6.0%) is less than that of the fluid coke (7.0%), which means less sulfur is emitted during the production process.
3. The heating value of delayed coke (34.7 MJ/kg) is higher than that of fluid coke (29.7 MJ/kg). This has positive implications for using spent activated coke as a fuel source for generating energy.

Delayed coke samples were dried in batches of 100 to 200 g in a vaccum oven for 24 hours at a temperature of 110°C prior to grinding. Samples were pulverized using a ball mill and coke between 200 mesh (75 µm) and 325 mesh (44 µm) was utilized for the carbonization/activation experiments.

Carbonization and activation procedures

Production of the activated petroleum coke involved two stages: the carbonization or pyrolysis stage and the activation stage. The carbonization stage was carried out at 850 ± 2°C at an average heating rate of 10°C/min. The activation stage was carried out immediately after carbonization, i.e., once the temperature reached 850°C, using steam. Activation periods, or soak times, of two and four hours were tested. All carbonization and activation experiments occurred in a horizontal quartz reactor (45 mm I.D.). The reactor was placed horizontally in a tube furnace with an accurate temperature controller and with a N_2 atmosphere.

The carbonization/activation procedure involves placing a measured amount of coke in the reactor. A metal thermocouple is inserted in one side of the reactor such that its tip is just above the coke sample. The reactor was sealed and purged with nitrogen gas, as illustrated in Figure 2. The experimental procedures are summarized as follows:

1. The powdered coke sample was placed in a ceramic boat and weighed, then placed in the reactor and sealed with a rubber stopper.
2. Nitrogen gas, at a flow rate of 20 mL/min, was used to purge the reactor at room temperature for at least two hours.
3. After purging the system, the carbonization stage was started by increasing the temperature at a rate of 10°C/min. The carbonization stage concluded when the temperature inside the reactor reached 850 ± 2°C.

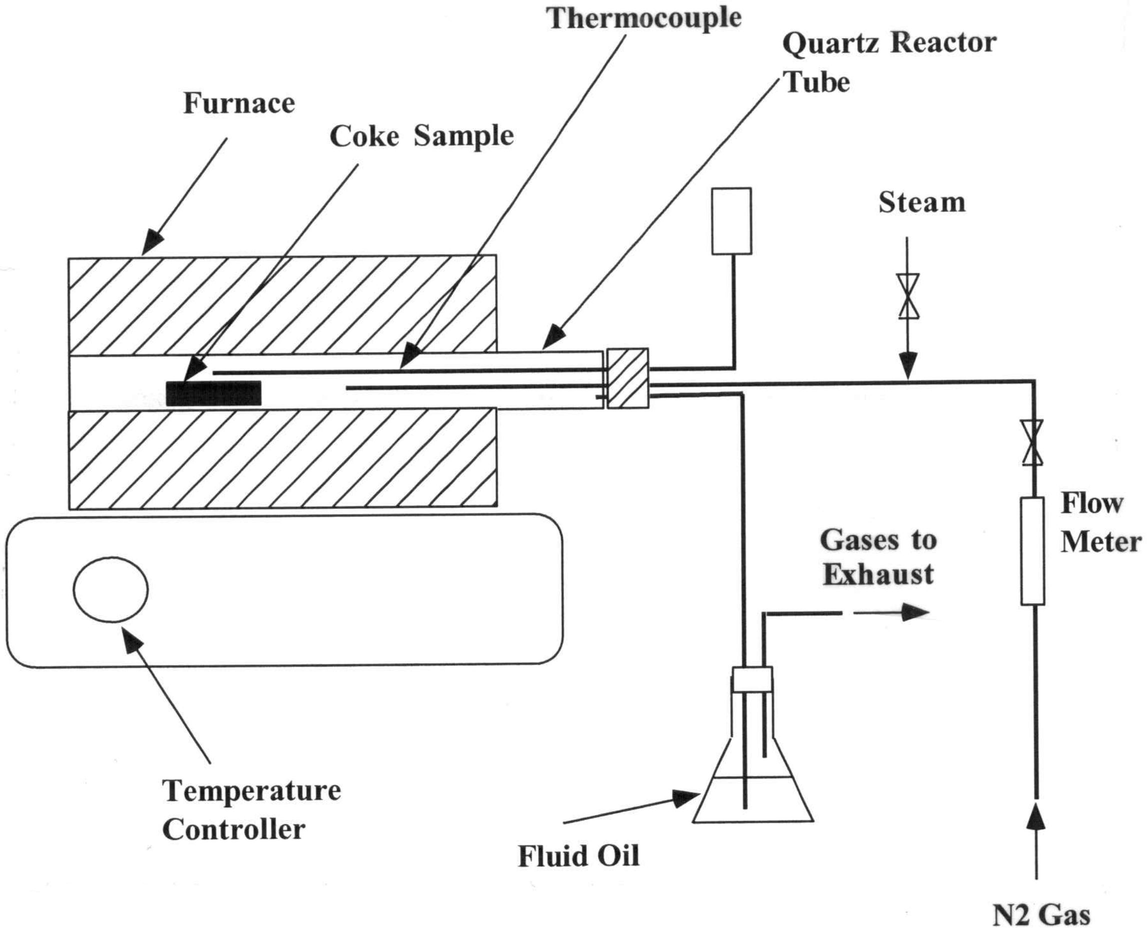

Figure 2. Experimental setup for the activation of petroleum coke.

4. The activation stage was started immediately by shutting off the N_2 flow and introducing steam at a flow rate of about 20 mL/min.

5. For the activation stage, two activation periods or soaking times of two and four hours were implemented.

6. At the conclusion of the activation stage, the power to the furnace was turned off and the reactor was allowed to cool down overnight under a flow of nitrogen.

7. The activated coke sample was removed from the reactor, weighed, and stored in glass vials until needed for testing. The recovery (R) was calculated by dividing the weight of the activated carbon by the original weight of the sample multiplied by 100%. Conversely, the burnoff (B) was calculated as 100% - R.

Evaluation of activated coke production using methylene blue adsorption

The activated coke samples were evaluated by performing liquid-phase adsorption using methylene blue dye as adsorbate. The procedure followed ASTM D3860-89a (Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique). Methylene blue adsorption is a quick experimental method that shows the ability of the activated carbon to adsorb large molecules that cause color in solution.

A methylene blue solution was prepared by dissolving 800 mg/L of dye into deionized water. The methylene blue concentrations in the tested samples were determined by spectrophotometry at 620 nm. After the adsorption test, the solution and the activated coke sample were filtered through Whatmann No. 42 paper filter. The absorbance of the solute was determined at 620 nm and the residual concentration of the methylene blue was calculated from a calibration chart. The results are expressed in terms of the amount of methylene blue adsorbed (in grams) per 100 g of activated coke.

Experimental Procedures for Adsorption Equilibrium

Adsorption isotherm tests were conducted to obtain an estimate of the capacity of activated coke for adsorbing color-causing compounds and chlorinated organic compounds such as chlorolignins. The adsorption isotherm experiments involved contacting the powdered activated coke with D_0 bleaching stage wastewater, obtained from the Weyerhaeuser Canada Ltd. mill in Grande Prairie, Alberta. The characteristics of the D_0 bleaching stage wastewater are given in Table 3.

Batch adsorption tests were carried out using the powdered activated coke (PAC) samples (samples activated for two and four hours) to generate the adsorption isotherms. For this purpose, 250 mL sealed flasks were filled with 100 mL of D_0 bleaching stage wastewater and different amounts of PAC were added. The mixture in each flask was mixed using a tumbler for 24 hours (assuming that the equilibrium was achieved in 24 hours). Subsequently, the wastewater was separated from the activated carbon by pressure filtration through Whatmann No. 42 paper filter. The filtrate was analyzed for color (measured at 465 nm), UV absorbance (measured at 254 nm) and AOX.

Table 3. D_0 bleaching stage wastewater characteristics.

Parameter	Concentration
COD	2126 mg/L
AOX	80.2 mg/L as Cl
$Color_{465nm}$	2300 mg/L Pt-Co
UV_{254nm}	13.110 cm-1
PH	2.1

4. RESULTS

Evaluation of the Production of Activated Coke

The methylene blue adsorption test is a quick and simple method for evaluating the success of activated coke production at different activation times. Raw petroleum coke adsorbed about 10 g of methylene blue per 100 g of carbon while a commercial powdered activated carbon adsorbed 32 g of methylene blue per 100 g of activated carbon. The methylene blue adsorption results for petroleum coke, activated coke and commercial activated carbon are shown in Table 4.

Activation of petroleum coke, using steam, increased its capacity for methylene blue adsorption. Also, increasing the activation time slightly improved the activated coke capacity for methylene blue adsorption. However, for the activation times evaluated in this study, activated coke had a lower methylene blue adsorption capacity than the commercially available activated carbon.

Adsorption Equilibrium Results

In these experiments, activated coke dosages ranged from 100 to 15,000 mg/L as shown in Table 5. Table 5 summarizes the results for remaining color, UV absorbance and AOX at different activated coke dosages and for two activation times.

The results show that in the carbon dose range of 100 to 1000 mg/L, the highest removal of color, UV absorbance and AOX was 22%, 12% and 26%, respectively, for an activation time of four hours. As the carbon dose increased from 5000 to 15,000 mg/L, higher removals were achieved: 93% for color and 87% for UV absorbance and AOX. Also, increasing the activation time of the petroleum coke from two to four hours resulted in a slight increase in the removal of color, UV absorbance and AOX for all carbon dosages applied in this study. The percentage reduction in color, UV absorbance and AOX as a function of carbon dosages and different activation times is illustrated in Figures 3 to 5.

Table 4. Methylene blue adsorption for different carbon sources.

Carbon Source	Grams of Methylene Blue Adsorbed per 100 g Carbon
Raw petroleum coke	10
Activated coke (activation time 2 hr)	25
Activated coke (activation time 4 hr)	27
Commercial activated carbon	32

Table 5 Adsorption isotherm results.

Activated Coke (mg/L)	Color $_{465\text{ nm}}$ (mg/L Pt)		UV $_{254\text{ nm}}$ (cm^{-1})		AOX (mg/L as Cl)	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
100	2047	1923	13.10	12.94	73.5	69.1
500	2013	1901	12.20	12.01	64.3	64.0
1000	1836	1787	11.87	11.53	63.1	59.1
5000	1197	1141	6.48	6.10	31.9	28.9
10000	821	458	3.22	2.54	19.9	19.3
15000	256	147	1.92	1.65	11.5	10.2

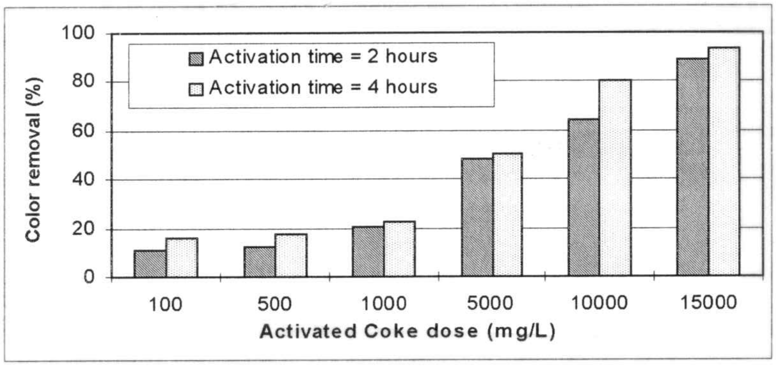

Figure 3. Color removal as a function of carbon dose and activation time.

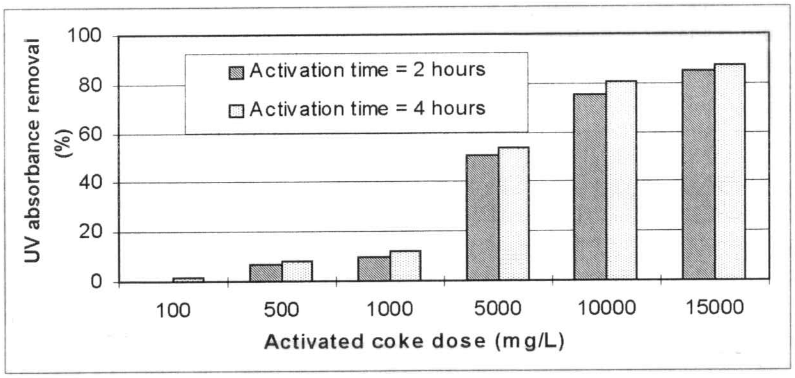

Figure 4. UV removal as a function of carbon dose and activation time.

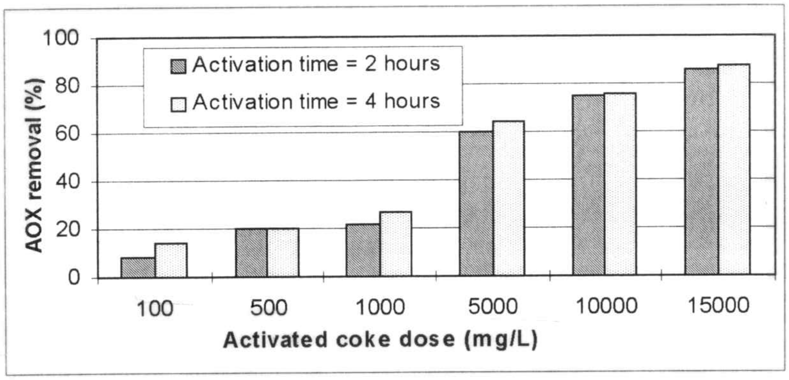

Figure 5. AOX removal as a function of carbon dose and activation time.

The adsorption capacity of activated coke with activation times of two and four hours was estimated from adsorption isotherm data for color$_{465}$. Color was selected because it correlates well with the concentration of high molecular weight chlorolignins (Çeçen, 1993). Adsorption data were best fitted by least square regression using the Freundlich equation of the form:

$q = X/M = K C_e 1/n$ (1)

where q is the amount of color adsorbed per gram of activated coke, X is the adsorbed amount of color, M is the weight of carbon, C_e is the equilibrium concentration of color in solution and K and 1/n are Freundlich adsorption parameters.

The Freundlich parameter K represents the adsorption capacity of the carbon for specific adsorbate, in this case chlorolignins, at a given equilibrium concentration, C_e. The term 1/n indicates the effect of concentration on the adsorptive capacity of the carbon. In general, a high value for both K and 1/n are desirable for higher color reduction.

Isotherm data for the activated coke with four hours activation time are summarized in Table 6. The data were plotted, as log q vs. log C_e, to generate the adsorption isotherm shown in Figure 6. Based on Figure 6, one can observe two distinct adsorption isotherms: a steep isotherm, or region 1, and a flat isotherm, or region 2.

Table 6. Adsorption isotherm calculations for four hour activation.

Carbon Dose, M (mg/L)	Equilibrium Color, C_e (mg/L Pt)	Color Reduction (%)	$X = C_I\text{-}C_e$ (mg/L Pt)	Q = X/M (mg/g)
100	1923	16.4	377	377
500	1901	17.3	399	80
1000	1787	22.3	513	51
5000	1141	50.4	1159	23
10000	458	80.1	1842	18
15000	147	93.6	2153	14

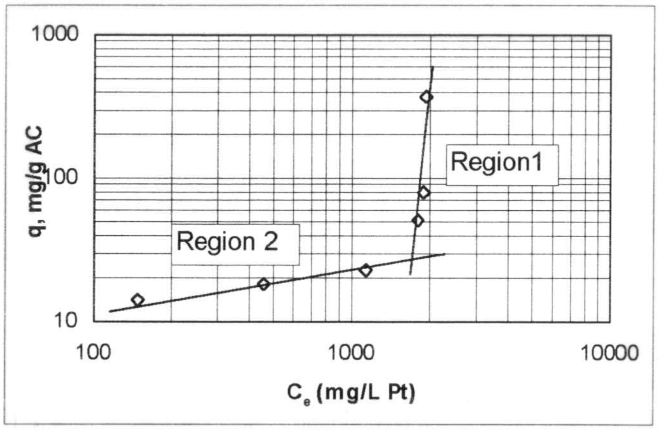

Figure 6. Isotherm equilibrium data for activated coke with four hours activation time.

At low carbon dosages from 100 to 1000 mg/L (region 1), the wastewater contained both easily and poorly adsorbable compounds, which compete for activated carbon sites. In this case only the easily adsorbable compounds are removed from the solution so the poorly adsorbable compounds left in the solution determine the equilibrium concentration. Thus a steep isotherm is obtained (Sontheimer et al., 1988).

As the carbon dose increases from 5000 to 15000 mg/L (region 2), the amount of easily adsorbable compounds per unit mass decreases. The isotherm flattens and reflects only the behavior of poorly adsorbable compounds, or the high molecular weight chlorolignins. Therefore, the Freundlich parameters were determined based on region 2 of the adsorption isotherm.

Table 7 summarizes the Freundlich parameters for activated coke, with activation times of two and four hours. The results indicated that both parameters increased as the activation time increased from two to four hours. That means the activated coke adsorption capacity for color and chlorinated organics increased with increasing activation time. However, for the activation periods investigated in this study, the capacity of activated coke for color and chlorinated organics was lower than that obtained from commercial activated carbon.

Table 7. Freundlich parameters.

Activated Carbon Source	K (mg/g activated carbon)	1/n
Activated coke (activation time = 2 hr)	3.17	1.58
Activated coke (activation = 4 hr)	4.50	4.29
Commercial activated coke	14.6	4.60

5. CONCLUSIONS

The preliminary results from this study confirmed that the activation process of petroleum coke, at a temperature of 850°C and using steam, was successful. The methylene blue adsorption results showed that higher amounts of methylene blue were adsorbed per 100 g of activated coke compared to raw petroleum coke. Also, the results showed that increasing activation time from two to four hours increased methylene blue adsorption.

The adsorption equilibrium experiment results showed that high color and AOX reduction of D_o bleaching stage wastewater was achieved using activated coke. An activated coke dose of 15,000 mg/L resulted in about a 90% reduction in color and 87 % reduction in AOX. Previous studies on the adsorption of nonbiodegradable matter in biotreated wastewater using different types of activated carbons showed that more than 90% reduction in color and AOX could be achieved when an activated carbon dose in excess of 10,000 mg/L was used (Çeçen, 1993). The adsorption results also showed that increasing the activation time from two to four hours increases color and AOX reduction.

The activated coke dosage required for high color reduction in bleached kraft mill wastewater is considered high, which raises cost concerns. However, the amount of color adsorbed per gram of activated coke is also relatively high. This can be seen when the amount of color adsorbed per gram of activated carbon used for color removal from bleached kraft mill wastewater is compared to that for river water. The amount of color adsorbed for the D_o bleached stage wastewater ranged from 140 to 180 mg/g of activated coke. On the other hand, the amount of color adsorbed for North Saskatchewan River water usually ranges from 300 to 350 mg/g powdered activated carbon.

Based on the encouraging results of this study, further research is required. Recommended research includes:

1. Optimization of the activation of petroleum coke for color and AOX reduction. This can be achieved by activating the coke at different steam-to-carbon ratios as well as for longer periods.
2. Adsorption kinetic studies are required to determine the time required for certain removal efficiencies of color and AOX. This information would aid in sizing the reactor used for mixing or contacting the activated coke and bleached kraft mill wastewater.
3. Evaluation of different methods of separating the spent activated coke from the wastewater, e.g., dissolved air flotation.
4. Evaluation of different methods of utilizing the spent activated coke, e.g., in direct combustion for steam generation.

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