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THE UNIVERSITY OF ALBERTA

SELECTION CRITERIA FOR POWDERED ACTIVATED CARBON FOR WATER TREATMENT

by

SUZANNE TROXLER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SELECTION CRITERIA FOR POWDERED ACTIVATED CARBON FOR WATER TREATMENT submitted by SUZANNE TROXLER in partial fulfilment of the requirements for ~~the~~ degree of MASTER OF SCIENCE in ENVIRONMENTAL ENGINEERING.

Daniel W. Smith

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Date June 29, 1987

ABSTRACT

Powdered activated carbon (PAC) is added at water treatment plants to improve the aesthetic quality of water, mainly by adsorption of the taste and odour causing compounds. Success in controlling the taste and odour episodes with PAC is dependent on the composition of the water, on the conditions under which PAC must adsorb and on the type of PAC applied. The most effective PAC will possess a high adsorptive capacity for the majority of organics of concern. In this study, the existing tests for the evaluation of PAC are examined and compared to adsorption isotherm tests using surrogate compounds, to determine an appropriate basis for PAC selection.

Six PAC samples were selected on the basis of their iodine number, their adsorptive capacity for tannic acid and their particle size distribution. Single-solute adsorption isotherm tests, using phenol, mesitylene and total organic carbon (TOC), as well as phenol in river water isotherms, were performed to compare the PACs and the adsorption tests.

Trends in the results allowed a general classification of the PACs into two groups, according to their capacity to adsorb high or low molecular weight compounds. It was found that the capacity to adsorb phenol can be measured by the modified phenol value test; using a lower initial concentration of phenol and river water as the background matrix did

not change the grading of the PACs. The tannin value test can give an indication of the capacity to adsorb TOC and humic substances. PACs with a high capacity for tannic acid adsorbed less phenol in the presence of TOC than other PACs. A comparison of the mesitylene isotherm and the phenol isotherms showed the possibility of a specific interaction between phenol and PACs with the appropriate surface chemistry.

Considering the variability in the raw water content, and the incomplete identification of the compounds which cause the taste and odour, the evaluation of PACs cannot be based on the specific problem-causing compounds. A testing protocol which makes use of the iodine number test, the modified phenol value and tannin value isotherms, supplemented by a mesitylene adsorption test, is recommended at this time.

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1. INTRODUCTION

In municipal water treatment plants, powdered activated carbon (PAC) is commonly added to the water to assist in the control of seasonal taste and odour episodes. PAC can be applied, dry or in a slurry, at various treatment stages before filtration: generally, when large doses of PAC are required, addition is made at the mixing basin; small amounts can also be applied at the filter influent. On average, dosages of 0.25 to 60 mg/L are added to treat surface waters. PAC has been used to adsorb organic compounds of biological origin, such as algae and bacterial metabolites, of anthropogenic origin, such as hydrocarbons from street runoff, industrial pollution and occasional oil spills, and naturally occurring organics, such as humic substances in an attempt to reduce the THM formation potential (AWWA, 1976). Although PAC is extensively used because of its non-specificity in adsorption, its operational flexibility, its low initial capital costs and the absence of by-products, its performance has been found to vary widely depending on the problem-causing organics, the plant treatment scheme, the conditions under which adsorption occurs and the type of PAC used.

At the City of Edmonton Water Treatment Plants, control procedures of the often highly offensive taste and odour occurrences consist of oxidation with chlorine dioxide in combination with adsorption with PAC. When conditions require the addition of PAC (street or watershed runoff, high turbidity and colour, taste and odour in the treated water, oil spills), a dosage of 5 to 20 mg/L is applied at the rapid mixing unit, concurrently with alum, chlorine dioxide and ammonia (Murdoch, 1985). Only limited success in reducing the taste and odour in the treated water has been achieved in the past (Walker *et al.*, 1986). During the spring runoff of 1986, increasing the chlorine dioxide dose did not reduce the odour; however, PAC addition was found useful in adsorbing the odour-causing compounds in the street runoff, consisting mainly of hydrocarbons (Hrudey, 1986). In an attempt to improve on their taste and odour control performance, the selection of a more efficient PAC is now sought.

The objective of this research was thus to determine the appropriate selection criteria which would ensure the purchase of a PAC with a high potential for removal by adsorption of the majority of organics of concern.

In order to achieve this objective, the main approach was to examine the existing tests for PAC and evaluate them by a comparison with isotherm adsorption tests using chosen surrogate compounds. The latter tests can then supersede or supplement the standard tests in a suggested testing protocol.

The research plan was to first conduct a review of the literature on the adsorption of organics on activated carbon and on the existing evaluation procedures for PAC. From a list of compounds which had been detected in the raw water during taste and odour occurrences in Edmonton, a surrogate chemical was selected on the basis of representativeness of a group of compounds and analytical feasability in a testing procedure. An adsorption test procedure using this selected surrogate compound, at conditions which approximate the actual conditions at the water treatment plants, was then prepared. All the available PACs were tested by appropriate standard test procedures in order to obtain a preliminary assessment of their adsorption capacity for both high and low molecular weight compounds. Selected PACs were then further evaluated by additional standard tests and for their adsorption capacity for the surrogate compounds. By comparison of the latter with the standard test results, the validity and usefulness of the existing testing procedures were assessed. A testing protocol which takes into account the established procedures, the extent of the knowledge of the complex raw water content and the need for a PAC which can adsorb a wide range of compounds could then be suggested.

2. LITERATURE REVIEW

The complex nature of activated carbon combined with the heterogeneity of water supplies brings about a broad range of application possibilities for PAC in the water treatment field. All organics can adsorb to a certain extent, under certain conditions, on activated carbon. An overview of the state of the art of organics adsorption on activated carbon was the first step in the determination of an appropriate basis for the evaluation and purchase of PAC for water treatment. This literature review covers the update knowledge of the nature and characteristics of activated carbon, the factors which influence the adsorption of organics on activated carbon, a few examples of PAC applications and finally, the existing testing procedures devised to compare PACs.

2.1 Manufacture and Description of Activated Carbon

Activated carbon is produced from carbonaceous raw materials such as bituminous coal, lignite, peat, wood, petroleum base residues and pulp mill wastes.

Typically, activated carbon prepared for water treatment applications is manufactured by "thermal" methods. That is, the raw material is slowly heated in the absence of air (pyrolysis) to a temperature usually below 600°C. The carbonisation residue called char, coke or amorphous carbon is then activated with an oxidizing agent such as steam or carbon dioxide at 500 to 900°C. Portions of the char are oxidized and released as gaseous oxides, forming hollow pores. This activation process can be carefully controlled to produce a well-defined pore system (Holden, 1982; Faust and Aly, 1983).

The resulting structure is composed of fused hexagonal rings of carbon atoms, called microcrystallites, grouped in thin planes stacked one over the other. This arrangement, however, is quite assymetric and shows numerous hollow pores. Chemically bonded elements such as oxygen, hydrogen and sulfur, arranged into functional groups or heterocyclic ring systems, mark the edges of the microcrystallites and interconnect the basal planes (Snoeyink and Weber, 1967; Faust and Aly, 1983). Depending on the temperature and type of oxidizing gas used in the activation process, two types of surface oxide functional groups can be present. Acidic surface oxides such as carboxylic, lactic and phenolic groups, are developed at low temperatures (200 to 400°C). Basic surface oxides such as carbonyl groups require higher temperatures (800 to 1000°C) for their formation (Cookson, 1978). Activated carbon contains an extensive network of interior pores. Macropores (diameter larger than 600 to 1000 Å) which are formed during carbonisation, resemble large capillaries from which mesopores (100 to 600 Å diameter) and micropores (diameter up to 100 Å) branch out. The micropores, created by the activation process, account for the very large internal surface area, characteristic of activated carbon (Weber, 1972; McGuire and Suffet, 1978; Holden, 1982; Faust and Aly, 1983).

2.2 Adsorption Process

The surface chemistry and pore structure of activated carbon make it an ideal adsorbent for the numerous organic contaminants in water. Its complexity also brings about a diversity of adsorptive reaction mechanisms.

Adsorption can be described as the process where ions or molecules are extracted from solution and concentrated at the surface of a solid or adsorbent (in the case of adsorption of a liquid on a solid). Adsorption is favoured if there is chemical incompatibility between the solute and the solvent and if the solute has an affinity for the adsorbent.

According to Weber (1972), three types of adsorption are generally recognized: physical, chemical and exchange adsorption. Physical adsorption is due to Van der Waals forces between the adsorbent and the adsorbate molecules. It is a fully reversible process, not site specific and usually predominant at low temperatures. Chemical adsorption involves the formation of true chemical bonding between the adsorbate and the solid at specific sites. It is an irreversible reaction, which permits no transmigration at the surface. Exchange adsorption involves the electrostatic attraction of ions to charged sites at the surface of the carbon. For most cases, all three types of adsorption can occur. Organics can also adsorb on carbon by specific interactions between structural elements such as functional groups.

Adsorption of a molecule from solution proceeds in three steps: 1- film diffusion which corresponds to the transport of the solute from the bulk of the solution to the surface of the carbon; 2- pore diffusion, where the solute moves within the pores of the carbon; 3- adsorption on an available site on the interior surface of a pore. In batch processes, where a high degree of agitation is maintained, pore diffusion is the limiting step (Weber, 1972).

2.3 Factors Affecting Activated Carbon Adsorption

2.3.1 Characteristics of Activated Carbon

The observed adsorption behaviour of activated carbon is partly the result of: its internal surface area, its pore size distribution, its particle size and its surface chemistry.

Surface Area

Activated carbon's high adsorptive capacity is mainly due to its large internal surface area or, more precisely, its accessible surface area, the area available for adsorption of a given compound. Most of the area is provided by the micropores, where most of the adsorption sites are located. In general, the carbon loading (amount adsorbed per unit mass carbon) is greater the finer and more porous the adsorbent (Weber, 1972). This is true only to a certain extent however; the adsorption of larger molecules can be significantly limited if the large surface area is caused by a predominance of very small pores. (McGuire and Suffet, 1978).

Pore Size Distribution

The pore size distribution has a significant effect on both the capacity and rate of adsorption. Although most adsorption sites are located on micropore walls, a sufficient number of macropores and mesopores is necessary to permit rapid diffusion of the solute to those sites, thus increasing the adsorption rate, and to accommodate all molecular sizes of adsorbable organic compounds (Weber, 1972; McGuire and Suffet, 1978).

This is also suggested by Borneff (1980) who, in his study of the adsorption of polyaromatic hydrocarbons (PAH), found that the rate of adsorption decreased as the molecular weight of the PAHs increased. He saw a dependence of the adsorption rate on the availability of pores which can accommodate the PAH's steric configuration.

In a study of humic and fulvic acid adsorption, Lee *et al.* (1981) concluded that the pore size distribution was an important parameter in determining the carbon's capacity for humic substances. Their conclusion was based on good correlations obtained between adsorption capacity and pore volume in pores smaller than a certain radius.

This was confirmed in an extensive study by Weber *et al.* (1983). Adsorption tests of commercial fulvic acid on three activated carbons showed that the adsorption capacity was greatest for the carbon with a predominant pore radius larger than 1000 Å.

Similarly, the results of Herzing *et al.* (1977) indicated that the activated carbon with the larger average pore size and with more surface area had a higher capacity for commercial humic acid.

Particle Size

In general, adsorptive capacity is relatively independent of particle size since the surface area providing adsorption sites is internal. While this is generally true, smaller particles obtained by the crushing of granular carbon exposes pores which might not have been otherwise accessible (Weber, 1972). If granular and powdered carbons are compared, PAC (90% of particles smaller than 0.15 mm) has more surface availability per unit weight carbon than GAC (particle size between 0.6 and 2.4 mm) (Cini *et al*., 1981).

Weber *et al*. (1983) found that the adsorption capacity for fulvic and humic acid increased the smaller the particle size. This observation can be explained by the slower rate of adsorption through larger carbon particles. Earlier work by Peel and Benedek (1980) suggested that phenol and o-chlorophenol isotherms were independent of particle size. They argued that if enough time is provided for equilibrium to be reached, the adsorption sites in the small pores of large carbon particles will eventually be filled.

Surface Chemistry

The adsorption of specific compounds from dilute solutions is influenced by the surface chemistry of activated carbon. It is agreed that surface oxides impart polarity to activated carbon and permit preferential adsorption of polar compounds. However, these surface functional groups can hinder the adsorption of most organics found in water. Water molecules will attach to these sites at the edge of the pores by a strong hydrogen bond, thus restricting access to the pores and reducing the number of adsorption sites (Snoeyink and Weber, 1967; Coughlin and Ezra, 1968).

Giusti *et al*. (1974) showed that an increase in surface oxides reduced the ultimate adsorption capacity of activated carbon for alcohols, ketones, aldehydes, esters and organic acids.

Acidic surface oxides were found to hinder the adsorption of anionic adsorbates, aromatics such as phenol and related nitrophenols, non-polar aliphatics such as decane, and humic substances (Coughlin and Ezra, 1968; Cookson, 1975; McCreary and Snoeyink, 1980). An excessive amount of acidic surface oxides can be formed by contacting activated carbon with chlorine (Cookson, 1975).

The presence of basic surface oxides can improve adsorption of acids and aromatics, particularly when there are substitutions in the ring. A donor-acceptor complex forms where the electrons are provided by the carbonyl oxygen on the carbon and the electron acceptor is the aromatic ring (Cookson, 1975).

It can therefore be seen that changes in pH will affect the nature of the activated carbon's surface chemistry and consequently cause variations in its adsorption capacity.

2.3.2 Properties of the Adsorbate and Conditions of the Solution

The extent and rate of adsorption on activated carbon also depends on the properties of the adsorbate and on the conditions under which adsorption will occur. Correlations between adsorption capacity and the properties of individual compounds such as solubility, molecular size and weight, functional groups and polarity have been found. Temperature, pH and competition effects in relatively simple systems have also been delt with. Many of these factors are interrelated.

Solubility

Solubility is the most important property affecting adsorption capacity. A highly soluble compound will not be easily adsorbed due to the presence of a strong solute-solvent bond which must be broken before adsorption can take place (Weber, 1972).

Giusti *et al.* (1974) studied 10 classes of compounds and found that the aromatics exhibited the greatest amenability to adsorption because of their relatively low solubilities in aqueous solution and π bonding to the aromatic surface of activated carbon.

Polarity

The polarity of organics affects their amenability to adsorption because it influences their solubility in water. In general, adsorption decreases with increasing polarity (Weber, 1972; Giusti *et al.*, 1974). Activated carbon produced for water treatment should be only slightly polar, or less polar than water, to increase the affinity of the majority of organics in water for the adsorbent rather than the solvent (water).

Molecular Size

The size of a molecule is important in PAC applications because a higher rate of adsorption can be expected with a small adsorbate since it has access to more pores more rapidly. This is in agreement with McCreary and Snoeyink (1980) who suggested that fulvic acid can move more rapidly in the pores than the larger humic acids. This explains why large molecules such as the higher molecular weight fraction of humic substances do not seem to be adsorbed to the same extent as low molecular weight fractions, with similar contact times (McCreary and Snoeyink, 1980; Lee *et al.*, 1981; Weber *et al.*, 1983).

A size exclusion phenomenon can however restrict large molecules from small micropores. Summers and Roberts (1983) normalized adsorption capacity results with respect to the accessible surface area and found a similarity of adsorption affinity among all macromolecular organic matter weight fractions.

On the other hand, a general tendency of increased adsorption capacity with an increase in molecular weight was found for 93 petrochemicals (Giusti *et al.*, 1974) and aromatics (Al-Bahrani and Martin, 1976; El-Dib and Badawy, 1979). This effect is explained partly by the decrease in solubility as the molecular weight of compounds in a series increases and by stronger Van der Waals forces due to the larger surface area they act upon (Martin and Al-Bahrani, 1979).

Degree of Ionization and pH

It has been repeatedly found that, for structurally simple compounds, charged species adsorb less than neutral species. Snoeyink *et al*. (1969) examined the adsorption of phenol and nitrophenol. They observed a reduction in adsorption of phenol at a pH above its pKa. It was explained by the repulsive forces between the anionic phenol and the negatively charged carbon surface and between the phenol molecules themselves.

Martin and Iwugo (1982) studied organics typical of wastewaters and concluded that more adsorption is achieved in the pH range which induces the most undissociated molecules. pH affects adsorption of ionized species quite significantly because of the strong adsorption of the H^+ and OH^- ions (Martin and Al-Bahrani, 1978; Martin and Iwugo, 1978). According to Faust and Aly (1983), the adsorption characteristics of weak organic acids follow a general pattern. Although both undissociated and ionized forms of a species can be adsorbed, the undissociated molecule is adsorbed more strongly. At a pH greater than the pKa, the adsorption capacity is greatly reduced. As the pH is lowered, the adsorption capacity increases. The rate of increase starts to decrease however, after reaching the pKa.

At pH values much lower than the pKa, adsorption capacity can decrease due to the competitive interaction between the hydronium ion and the carbon surface (negative surface charge).

For complex molecules such as humic substances, the effect of pH is difficult to predict. Weber *et al.* (1983) explained improved adsorption of humic acid at low pH by considering the humic acid as a mixture of compounds with weakly acidic functional groups which were mostly uncharged at low pH, therefore more adsorbable.

Boening *et al.* (1980) and McCreary and Snoeyink (1980) observed increased adsorption of humic substances with decreasing pH.

The effect of pH depends also on the surface chemistry of the activated carbon. Simply stated, if acidic surface oxides are present at the edge of the pores, an increase in pH can reduce the pore blockage. If the carbon has an overall negative charge, then decreasing the pH will neutralize the carbon and increase the adsorption capacity for typical pollutants by increasing the access to more surface area for adsorption.

Temperature

Faust and Aly (1983) state that since the adsorption process is spontaneous and there is always a decrease in entropy as a solute is adsorbed, the process must always be exothermic. A reduction in the equilibrium adsorption capacity is thus expected with increasing temperatures. However, usual temperature variations of the water do not affect the extent of adsorption significantly (Weber, 1972).

The rate of adsorption is dependent on temperature and follows the Arrhenius equation. The kinetics of adsorption are more rapid at higher temperatures (Dedrick and Beckmann, 1967; Weber, 1972).

Competition Effect

The adsorption behaviour of organic contaminants in a mixed-solute system such as raw water cannot be predicted based on the general trends described in the previous paragraphs. Numerous studies have confirmed that the presence of other solutes competing for adsorption sites depresses the rate and capacity for adsorption of individual compounds (Weber and Morris, 1964; Herzing *et al.*, 1977; Giusti *et al.*, 1974; Martin and Al-Bahrani, 1977; El-Dib *et al.*, 1978; El-Dib and Badawy, 1979; Smith and Weber, 1985). In summary, the inhibition of adsorption is a factor of the relative molecular sizes of the molecules, the relative adsorption affinities, the relative concentration of the solutes and the number of solutes (Weber and Morris, 1964).

In a study of bi-solute systems of low molecular weight aromatics (Martin and Al-Bahrani, 1979), 3 out of 4 systems showed that the higher molecular weight compound was more favourably adsorbed due to a higher affinity of the larger molecule to the carbon surface. This study also revealed that compounds with similar adsorbability in single-solute solutions did not have similar capacities in bi-solute solutions.

In a previous paper, Martin and Al-Bahrani (1977), studying the same compounds, found that the less effectively adsorbed the compound, the more adversely it was affected by competitive adsorption. They also showed that the effect of competition became more pronounced with an increase in the number of solutes.

However, Weber and Morris (1964) measured a combined rate of removal of all organic matter (in bi-solute systems) greater than the rate of either solute in a single-solute system due to an increase in overall diffusion pressure, caused by a higher initial concentration.

More importantly for water treatment, and as expected, the presence of dissolved organic matter, generally in high concentration relative to the organic contaminants of concern, has a negative impact on the adsorption of potentially hazardous organics. This was suggested by Weber and Morris

(1964) for the adsorption of taste and odour causing compounds and verified by Herzing *et al.* (1977) for the adsorption of geosmin and MIB (2-methylisoborneol). The competition effect varies however with the class of compounds. The least impact was observed for the benzenoid compounds represented by p-dichlorobenzene, naphthalene and phenol in the study by Smith and Weber (1985). They also noted that certain organic pollutants can associate with humic substances and exhibit different adsorptive characteristics than they would in their absence.

Effect of Alum

Addition of PAC prior to coagulation to take advantage of the rapid mixing and sedimentation contact time may also reduce the carbon's adsorption capacity and rate.

Gauntlett and Packham (1973) in comparing the adsorption rate of chlorophenol in the presence of 20 mg/L alum and without, with a PAC dosage of 10 mg/L, have suggested that the observed reduction in adsorption rate was due to the coating of the carbon particle with the alum floc.

Similarly, at the East Bay Municipal Utility District, PAC (5 to 30 mg/L) was found relatively ineffective in removing THMs and TOC. Carns and Stinson (1978) hypothesized that maybe the PAC particle served as a nuclei for flocculation in the presence of alum (17 mg/L). The floc growth on the particle may have shielded the carbon from the dissolved organics.

Cini *et al.* (1981) generalized that the concurrent use of coagulants and PAC reduces the adsorption capacity of PAC because of the greater quantity of organic material and the competitive effect.

However, contrary to expectations, a recent study by Lalezary *et al.* (1986) presented data indicating no detrimental effects of alum and polymer addition on the adsorption of taste and odour causing compounds (including geosmin and MIB). In their experiments, PAC dosages up to 20 mg/L were contacted for three hours with 100 ng/L of selected taste and odour causing compounds, in the presence of 10 mg/L alum, 1 mg/L chlorine and 1 mg/L polymer.

2.4 PAC Applications

Powdered activated carbon has been applied at municipal water treatment plants since 1930. Bench-scale and full-scale experiments conducted by Spalding at the New Milford Treatment Plant in New Jersey, demonstrated that small amounts of pulverized "activated char" added with the alum coagulation process could remove odours due to microorganisms, phenolic substances and the "ordinary odor-producing substances present in surface water" (Spalding, 1930). By the end of 1931, about 150 water treatment plants had tried

PAC and in 1941, 1200 plants reported using it to control taste and odour occurrences.

Earlier experiments with granular activated carbon units had been initiated in 1928 by Baylis who proved they could be successful in removing phenols and excess chlorine (from superchlorination). The first full-scale GAC filters for municipal water treatment in the United States were installed in Bay City, Michigan in 1930, following the success of similar units at the Hamm Water Works in Germany in 1929 (Hassler, 1941).

A 1976 American Water Works Association (AWWA) survey of municipal water treatment plants in the United States showed that 25% of respondents used PAC only, to control organic contaminants, an additional 8% used PAC in combination with either chemical oxidation, granular activated carbon or both, for the same purpose (AWWA, 1977).

Addition of activated carbon at water treatment plants in Canada and the USA has been found useful in the removal of taste and odour causing compounds such as geosmin and MIB, THM precursors, TOC and trace organics (AWWA, 1976). However, success in reducing the organic content by PAC addition depends on many factors, not the least, the cause of the problem and the overall treatment scheme at the plant.

2.4.1 Case Studies

Case studies of full-scale, pilot plant-scale and bench-scale experiments or experiences with PAC are described to illustrate the variety of PAC applications at municipal water treatment plants.

Lalezary *et al.* (1985) reported pilot plant studies to optimize the adsorption by PAC of geosmin and 2-methylisoborneol (MIB), compounds produced from actinomycetes and algae, and known to cause earthy and musty odours at low concentration levels. The PAC, Calgon WPH, was applied concurrently with alum, a cationic polyelectrolyte, chlorine and aqua ammonia (chloramination). Four carbon dosages were studied: 5, 10, 15 and 23 mg/L. Results indicate that an initial concentration of up to 66 ng/L of each geosmin and MIB could be reduced to 2 and 7 ng/L, respectively, with a PAC dose of 10 mg/L. At more typical concentration levels, 22 ng/L of each compound, similar residual concentrations could be obtained with a PAC dose of 5 mg/L. However, they found that the presence of chlorine residuals reduced PAC adsorption, particularly when low PAC dosages were applied. With a 150 ng/L initial solution and 5 mg/L PAC, removals dropped from 51% to 26% for MIB and from 82% to 51% for geosmin, when 2 mg/L chlorine was present. The natural background organics caused an even more significant decrease in adsorption capacity, particularly at low PAC dosages. An increase in PAC dosage appeared to compensate for the competition effect. One hour contact time was provided for adsorption. Trials with longer retention times (4 hours) indicated that slightly better removals were obtained for low carbon doses.

Two periods of unacceptable taste and odour in the drinking water occurred in Philadelphia during 1985 (Burlingame *et al.*, 1985). The cause of the second occurrence was traced to the presence of a bed of blue-green algae in the Schuylkill River, producing high levels of geosmin. A taste and odour control program based on instrumental and sensory analyses permitted efficient management of the episodes at the Belmont Plant. Concentrations of geosmin up to 100 ng/L were detected in the river. The strategy to reduce the concentration to the target level set at 30 ng/L included treatment with PAC and the application point of chlorine moved forward; changes in intake pumping, dilution of water treated at the plant with other waters in the distribution system and source control. The PAC, Calgon WPH, dosed from 6 to 42 mg/L, was fed at the rapid mix. Analysis of the effluent showed that 12 mg/L PAC added at the same time as chlorine reduced the geosmin concentration by an average of 43%, while an application of 42 mg/L PAC prior to chlorination adsorbed 73% geosmin (73 ng/L to 20 ng/L). Taking into account the hydraulic modifications, up to 84% reduction was achieved.

Singley *et al*. (1979) described the results of a plant scale study to evaluate the effectiveness of various dosages of PAC to remove synthetic organics from a well field water supply in North Miami Beach. Dosages of 7.5, 15 and 30 mg/L of the PAC Hydrodarco B were fed at the well field , thus permitting 2 hours contact time. Their results show that THM precursors were removed much more efficiently than THMs. Volatile halogenated aliphatic organics showed only a slight decrease in concentration with dosage, while excellent removals of non-volatile synthetic organics was achieved: less than 5 μg/L remained after contacting 44 μg/L with 15 mg/L PAC. The TOC concentration was only reduced from 15 to 10 mg/L, but moving the chlorination point to the recarbonation unit improved TOC adsorption: with 7.1 mg/L PAC, TOC was reduced from 12.6 mg/L to 4.4 mg/L. Influent and effluent organics were then monitored with a constant addition of 7.1 mg/L PAC. It was observed that volatile organics were not being removed while the non-volatile organics were reduced by 95%.

Part of a bench-scale study of existing treatment processes, reported by Argaman *et al*. (1984), investigated the addition of PAC (Nuchar SA). The analysis included colour, TOC and the THM formation potential (THMFP). Large concentrations of PAC (10,000 mg/L) were required to reduce the colour to 20 Co-Pt units (raw water: 350 Co-Pt units), the TOC concentration to 3 mg/L (from 48 mg/L) and the THMFP to

265 μg/L (from 1,295 μg/L). When the PAC was added to treated water, a dosage of 10,000 mg/L was still necessary to achieve a water quality closer to the recommended maximum contaminant level (MCL) for colour (15 Co-Pt units) and THM (100 μg/L). A more typical carbon dosage of 50 mg/L achieved only 14.3% reduction in colour and 25% reduction in TOC.

2.5 Performance Evaluation of PAC

The evaluation of commercial PACs for purchasing and subsequent quality control has been a problem since the beginning of PAC addition for water treatment to reduce tastes and odours. Knowledge of the adsorption process, of the factors influencing it, and of models for the prediction of organics removal by adsorption, is now much more developed. However, applications of this knowledge to the problem of selecting the best PAC for water treatment is limited.

In the past 20 years, a few researchers have looked into comparisons of activated carbons with respect to their surface properties and adsorption capacity for specific compounds. The effects of the surface chemistry (Giusti *et al.*, 1974; Snoeyink *et al.*, 1969), the pore size distribution (Boening *et al.*, 1980) and the total surface area (Lee *et al.*, 1981; McCreary and Snoeyink, 1977) on the adsorption capacity have been mentioned. However Weber (1985) summarized the obvious conclusion in stating that the order of relative effectiveness of PACs will change from compound to compound.

Therefore, it is not surprising that municipal utilities must still make decisions for PAC selection and purchase based on standard tests devised more than 50 years ago.

Activated carbon manufacturers use a variety of tests and parameters to demonstrate the applicability of their carbons. The most common parameters are the apparent density, the particle size distribution and the ash and moisture content. The total surface area, the total pore volume or the pore volume distribution appear rarely in PAC specifications since their measurement require somewhat sophisticated equipment. Instead, manufacturers provide standard test values to give an indication of the structure of the PAC and mainly to show the adsorption capacity of PACs for a certain type of compounds. The iodine number and the modified phenol value tests are recommended by the AWWA Standard for PAC, therefore are always included in commercial PAC literature. Other tests such as the molasses number, the decolourizing index and the methylene blue adsorption test, remnants of the specifications for decolourizing carbons, are sometimes included. The tannin value test is considered optional by AWWA and is not generally provided. The threshold odour test is not used as a purchase criteria but rather for monitoring purposes. The above-listed tests are described in the following subsections.

2.5.1 Iodine Number

The iodine number is defined as the amount of iodine adsorbed per gram carbon when the residual iodine solution normality is 0.02N. It is a single-point adsorption test, that is, only one dosage of carbon is contacted with the aqueous iodine-potassium iodide solution. Iodine is adsorbed very strongly as free iodine or potassium tri-iodide (Sigworth, 1972).

Chaney *et al*. (1923), in their work on the nature of active carbon and their search for quantitative criteria of the adsorptive capacity found that the iodine number (which they term the activity of carbon) could replace the time-consuming determination of retentivity values. The latter criteria had been devised from the tube tests developed as specifications for gas-mask carbons. Retentivity was defined as the weight of adsorbed gas not desorbed after passing air over the carbon. A highly active carbon could adsorb 90% of the 0.2N iodine-potassium iodide solution in 3 minutes.

Chamberlain and Buckley (1925) considered a procedure based on the removal of iodine from solution and measurement of the residual iodine by a sodium thiosulfate titration, as more accurate than the other tests (dye tests) in the determination of the decolourizing capacity of carbons. The test they describe is in fact better than the test currently applied. They used a range of carbon dosages (0.05 to 1.0 g. PAC), they only used the carbon fraction passing a #300 mesh sieve, they ran a blank and the mixture was agitated for 3 minutes rather than 30 seconds.

An iodine value test is described in the Food Chemical Codex (1981). Measurement of the mass of iodine adsorbed by 100 g of "test substance" is used as an indicator of unsaturation.

According to Kipling (1967), the adsorption of iodine from aqueous potassium iodide solutions has been measured by many authors to determine the surface area of porous carbons and especially to follow changes in surface area as the surface chemistry of carbon is modified.

Juhola correlated the iodine number with the surface area of carbon pores larger than 10 Å (small micropores) (Lee *et al.*, 1981).

The carbon manufacturer, Westvaco, claims that a high iodine number expresses a large surface area for adsorption. A rule of thumb exists which states that 1 mg iodine adsorbed corresponds to 1 m^2 surface area as measured by the BET method (the Brunauer, Emmett and Teller method is based on the adsorption of a monolayer of nitrogen gas).

The iodine number is now widely accepted as a "broad spectrum" general purpose test to screen out carbons for water purification (Hassler, 1974).

2.5.2 Phenol Value

The phenol value test measures the capacity of an activated carbon for phenol, a low molecular weight aromatic compound (M.W.: 94.1), at a residual concentration of 10 µg/L. The phenol value stands for the concentration of carbon required to achieve 90% reduction in phenol concentration.

The phenol value test was recommended in the early days of PAC applications for water treatment as a test of the adsorption efficiency of PAC for taste and odour removal and as a criteria in purchasing specifications (AWWA, 1938). There was however an ongoing discussion between the advocates of the threshold odour test and the defenders of the phenol value test.

In 1937, Besozzi and Vaughn, in reporting the Hammond, Indiana experience with PAC, decided the phenol value test was the best known method to date to evaluate PAC for taste and odour removal, and used it as the sole criteria in their PAC purchase specifications. They considered the phenol value to be a measure of the activity of a carbon and its ability to adsorb odour.

Braidech (Besozzi and Vaughn, 1937) agreed that the phenol test could be used as quality control criteria, but it could not take into account the variety in quality and intensity of the tastes and odours encountered. It should thus be supplemented by the threshold odour test.

Helbig (1938) described the perceived weaknesses of the test. He mentioned the fact that tastes and odours may not be caused by phenol or phenolic compounds; the adsorption of odour does not always correspond to the adsorption of phenol; the contact time for the test is longer than actual plant conditions and the test solution has a low odour intensity.

Billings (1938) was concerned that since taste and odour varied locally, the test may not be practical if the best phenol value carbon does not designate the carbon which removes the most odour.

Sigworth (1939) advised that the phenol value not be considered as indicative of the efficiency of carbons in removing odours from water.

Although Welch (1939) agreed there was no definite relationship between the phenol value and the ability to remove taste and odour, it was still the best chemical method of determining the inherent activity of activated carbon and could serve as a "measure of the extent to which activation has been carried, insofar as ability to remove phenol".

It is reported by Sontheimer (1979) that in 1955, in Germany, the criteria to select grades of carbon for taste and odour removal was a good phenol value. The carbons thus chosen had only small pores and a small surface area. However in later years, as the demand on the carbon changed, new types of carbons with higher activity and surface area had to be used. A 1972 study by Sontheimer and Maier found that the phenol value was not a good indication of effectiveness for the adsorption of total organic matter (measured by UV at 240 nm) (McCreary and Snoeyink, 1977).

The AWWA standard specifications for PAC released in 1951 contained both the phenol value test and the threshold odour test. The phenol value test was later modified to reduce the test run time and because it was found to be sensitive to interferences in the lab. In the 1978 AWWA Standard, the modified phenol value test uses an initial phenol concentration of 200 mg/L.

2.5.3 Threshold Odour Test

The performance of carbons in the removal of taste and odour causing compounds can be determined by the threshold odour test. A threshold odour number (TON), the dilution of test water with odour free water at which the odour is just detectable, is measured by a trained panel for a predetermined range of carbon dosages.

The test was recommended by the AWWA in its report on the specifications and tests for PAC in 1938, to supplement the phenol value test, on the grounds that the test is capable of practical application in the control of taste and odour and in the evaluation of competitive carbons.

This opinion was not shared by Besozzi and Vaughn (1937) who argued that due to the great variability of water quality, a threshold odour test run at the time of purchase may not be indicative of the performance of the tested carbon later during the year. They also mentioned that the test could not be written in a contract as a quality control or purchase criteria. However the test was found very useful to monitor the performance of PAC and to determine carbon dosages, at the water treatment plant.

Helbig (1939) also realized that a similar TON may be caused by very different concentrations of odour causing compounds. Therefore, an adsorption test based on a fixed residual TON could not be used to compare PACs.

However Helbig (1938), Welch (1939) and Sigworth (1939) considered that since the actual water to be treated was tested, for the removal of odour, rather than a surrogate organic compound, the threshold odour test gave a true evaluation of PAC performance and had a much greater value than the phenol test.

The threshold odour test is now included in the 1978 AWWA Standard for PAC although it is not considered a sufficiently reproducible index of the performance of carbons.

2.5.4 Tannin Value

The tannin value is defined as the dosage of activated carbon required to reduce a standard 20 mg/L tannic acid solution to 2 mg/L (90% reduction).

This test is performed to evaluate the performance of activated carbons in removing large molecules such as the naturally occurring organics found in river water (tannins, lignins and mostly humic and fulvic acids). Tannic acid (gallotannic acid, $C_{76}H_{52}O_{46}$) is the commercially available substitute for tannin used in this adsorption test. It is not known how similar they are. The test is described by AWWA in its Standard for PAC (1978), but no minimum requirement for the tannin value has been set. It is considered optional.

2.5.5 Molasses Number, Value and Decolorizing Index

In this test, the adsorption of blackstrap molasses, the heavy, highly coloured effluent from the refining of cane sugar, is measured. It was devised by the sugar industry to evaluate decolourizing activated carbons for their treatment process. It's function can be extended to measure the adsorption capacity for high molecular weight compounds, for a wide range of applications.

Three variations of the test exist: the molasses number, the molasses value and the molasses decolorizing index. The molasses number is the mass of carbon required to reduce the colour of a molasses solution to the same value as obtained by a standard carbon. It is calculated from the ratio of optical densities of the residual filtrates. The molasses value is similar to the molasses number. It is obtained by comparing the adsorption of molasses by the carbon tested and the adsorption of a standard molasses solution by a standard carbon. The decolorizing index is the ratio of the molasses adsorption capacity of a carbon to that of a standard carbon times 10. It is obtained from a standard curve of optical density versus the decolorizing index of a standard carbon (USEPA, 1973).

2.5.6 Methylene Blue Adsorption

The methylene blue number is the mass of methylene blue ($C_{16}H_{18}N_3ClS$: M.W.: 319.9) adsorbed by 1 g of PAC at a residual concentration of 1 mg/L. This test was also invented to screen decolourizing carbons. Testing for the adsorption of the dye methylene blue is now performed to determine the capacity of activated carbons for larger molecules.

3. EXPERIMENTAL PROCEDURES

3.1 Introduction

The major suppliers and manufacturers of activated carbon products were contacted by letter to obtain the typical characteristics of the powdered activated carbons they produce (or supply) and a small sample for testing. Seven companies replied and 12 samples of PAC were received (see Table 3.1). The complete addresses of these manufacturers and their suppliers are listed in Appendix 1. The specifications and typical properties of the available PACs, as given by the manufacturers, are compiled in Appendix 2.

Eleven samples were initially tested to verify their specifications and to determine which PAC would be studied further. The twelfth, Cecarbon PAC 200 is typically applied to treat dry cleaning and metal plating effluents rather than for drinking water treatment. Consequently, it was not included in the screening. The PAC samples were screened on the basis of their particle size distribution and their capacity to adsorb low molecular weight compounds and larger or more complex molecules. Accordingly, the standard tests: particle size analysis, iodine number and tannin value, were chosen. The methods, apparatus and reagents for these tests are described in section 3.3.

Table 3.1 List of PACs received

MANUFACTURER	PAC
Westvaco Chemical Division	Aqua Nuchar Aqua Pac
Calgon Carbon Corporation	WPH WPL
Husky Charcoal Sales Inc.	Watercarb Watercarb Plus
American Norit	Darco S-51 Hydrodarco B
Norit Activated Carbon	Norit W-20
Atochem Inc. Ceca Division	PAC 20B PAC 200
Transpacific Carbon Co.	WTC

From this preliminary screening step, six PACs were selected. They were tested for the adsorption of phenol, mesitylene and total organic carbon (TOC). The phenol tests included an isotherm test at a high initial concentration - the modified phenol value test - and two isotherm tests at a lower initial concentration (10 mg/L), one in deionized water, the other in river water. The second stage of testing is described in section 3.4. Some characteristics and properties of the compounds used for screening and testing are compiled in Table 3.2.

3.2 General Procedures

For all tests, the solutions were prepared with freshly deionized water. A Milli-Q™ water system deionizes and removes organics from the on-line distilled water. The system consists of an activated carbon cartridge, two ion exchange cartridges and a Organex-Q cartridge (mixed-bed resins and activated carbon) placed in series. A GC/MS analysis of a direct injection of the Milli-Q™ water did not reveal the presence of any organics.

Chemicals used in the following experiments were all reagent-grade or better. Methanol (Fisher, 99.9%), the solvent used for the preparation of the mesitylene stock solution, was either triply distilled through a 0.5 m distillation column or doubly distilled through a 1 m long column. Its quality was checked using a gas chromatograph

Table 3.2 Physical characteristics and properties of the test compounds

Test Compound	Molecular formula	Molecular weight (g/mole)	Boiling point (°C)	Solubility water, 20°C (mg/L)	pKa
Iodine	I_2	253.809	184.35	290	--
Tannic acid (gallotannic acid)	$C_{76}H_{52}O_{46}$	1701.24	--	soluble	--
Phenol	C_6H_5OH	94.11	181.7	82 000[b]	9.9[a]
Mesitylene (1,3,5 Trimethyl-benzene)	C_9H_{12}	120.20	164.7	20[b]	--

reference: "CRC Handbook of Chemistry and Physics" (1981-1982)

[a]: Snoeyink and Jenkins (1980)

[b]: "Solubilities of Inorganic and Organic Compounds Vol.I" (1963)

with a flame ionization detector (GC-FID) under the conditions set for mesitylene analysis.

All glassware and Teflon was washed (dishwasher) in distilled water, rinsed with deionized water, oven-dried for a few hours and brought to room temperature prior to use. Glass carboys and pump tubing were repeatedly rinsed with distilled water and distilled methanol, then given a final rinse with deionized water.

3.3 Screening

3.3.1 Particle Size Analysis

The standard method to determine the particle size distribution of granular activated carbons (AWWA B604-74), the dry sieve analysis, was followed.

Between 50 and 100 g of each PAC was weighed in a tared dish, then dried at 140°C for at least 3 hours, cooled in a dessicator and reweighed to calculate the moisture content of the sample.

This exactly weighed amount of dry sample was placed on a stack of 3 preweighed sieves and a pan, mesh sizes 100, 200 and 325 (mesh openings 149 μm, 74 μm and 44 μm, respectively), covered and sieved using an electrically driven sieve shaker with an automatic timer set at 10 minutes

(Pascall Eng.). The sieves and bottom pan were then re-weighed.

The percent mass of carbon passing each sieve was calculated from the mass retained on each sieve and bottom pan.

The carbon fractions passing the 325 mesh and the fractions retained on the 325 mesh were dried again and stored separately in air-tight glass vials with Teflon liners, kept in the dark.

3.3.2 Iodine Number Test

The procedure for the iodine number test is described in the AWWA B600-78 Standard.

In this method, 6 to 7 g of each PAC was dried at 140°C for at least three hours and cooled in a dessicator.

An iodine solution, 0.05M iodine (I_2; Fisher,Laboratory grade) and 0.115M potassium iodide (KI; Fisher,Certified ACS), was standardized by titrating against 0.1N sodium thiosulfate ($Na_2S_2O_3.5H_2O$; Fisher,Certified ACS). The sodium thiosulfate was standardized beforehand against 0.1N potassium bi-iodate ($KH(IO_3)_2$; Fisher,purified).

For each PAC, three Erlenmeyer flasks, containing a weighed-in amount of carbon (between 1 and 2 g) were prepared. To each flask, 10 mL of 5% by weight hydrochloric acid (HCl) was added to wet and acidify the carbon. The content of the flasks was allowed to boil for 30 seconds and cooled to room temperature. A 100 mL aliquot of the standardized iodine solution was pipetted in each flask. The flasks were stoppered and vigourously shaken by hand for exactly 30 seconds. The content was then immediately gravity filtered (Whatman #2 filter paper), discarding the first 25 mL. The filtrate was mixed, 50 mL pipetted in an Erlenmeyer flask and titrated with standardized sodium thiosulfate, using starch as the end point indicator, until the blue colour just disappeared. From the titration, the residual iodine filtrate normality was calculated, and using the normality of the standardized initial iodine solution, the amount of iodine adsorbed was determined.

3.3.3 Tannin Value Test

A jar test procedure described in the AWWA B600-78 Standard was performed for the tannin value test.

First, a 15 L batch of 20 mg/L tannic acid (gallotannic acid, $C_{76}H_{52}O_{46}$; Baker Analyzed Reagent) in a sodium phosphate dibasic (Na_2HPO_4, Fisher Certified ACS) buffer solution (0.078M) was prepared, a volume sufficient to run 3 jar tests. The pH of the buffer was adjusted to 6.5 with phosphoric acid.

For each test, six 1 L square jars were filled with 800 mL tannic acid solution, measured with a graduated cylinder, and placed on a paddle stirrer. Five dosages of "as received" PAC, ranging from 50 to 400 mg/L, were accurately weighed in aluminum foil pans and poured into the jars. The sixth jar, the blank, contained the tannic acid solution only. The carbon/tannic acid solution mixture was mixed at 100 rpm for 1 hour. Approximately 200 mL was then vacuum filtered through a 0.45 μm cellulosic membrane filter (Micron Sep), discarding the first 25 mL. The filtrate was transferred to a labelled 250 mL glass screw-cap bottle for analysis.

The residual tannic acid concentration was determined by measuring the absorbance at a wavelength of 275 nm, with a UV-visible spectrophotometer (Pye Unicam SP8-400). A standard curve of tannic acid in the phosphate buffer solution was prepared to cover the concentration range 2 to 20 mg/L. A plot of this calibration curve is shown in Appendix 3. The instrument was zeroed with the buffer solution.

This procedure was followed for the eleven PAC samples. The test was repeated for the carbons which adsorbed less than 90% of the initial tannic acid solution. However, in these repeat experiments, the range of dosages was increased to ensure that a 2 mg/L residual tannic acid concentration was achieved. The dosages were determined on the basis of the results of the first experiment.

3.4 Testing

3.4.1 Selection of Testing Compounds

From the screening test results, six PACs were selected (according to a rationale described in section 4.2.4) which would be studied further for their capacity for adsorption of specific organic compounds. To determine which water contaminants would serve as the testing compounds, the 1986 GC/MS analyses of Rossdale and E.L.Smith raw water samples, taken when spring and street runoff were in effect, and previous lists of compounds detected in the raw water, provided by the City of Edmonton, were examined. [illegible] compounds were agreed upon by the City of Edmonton [illegible] University of Alberta. They were: hexadecane and [illegible]hylbenzene, organics typical of street runoff, and benzoic acid and an aldehyde such as isobutyraldehyde, 2-methylbutyraldehyde or isovaleraldehyde, which were found in river and treated water during upstream runoff.

To test carbons using a mixture of these compounds was considered impractical. Complex and time-consuming analytical procedures would be required to quantify accurately the amount of each of these compounds adsorbed per mass PAC, because of their wide range of solubiliy and volatility. To facilitate the analytical procedure and keeping in mind the basic requirement for a good testing protocol, simplicity, it was decided to run single-solute isotherm experiments.

The aldehydes, which are thought to be present in treated water during spring runoff, were considered too volatile (boiling point of isobutyraldehyde: 61.5°C, 2-methylbutyraldehyde: 92°C). The adsorption of benzoic acid is negligible. At pH 7.0, with an initial concentration of 10 µg/L, more than 100,000 mg/L PAC is required to reduce this concentration to 1 µg/L (Dobbs and Cohen, 1980). Moreover, adsorption of benzoic acid (pKa: 4.2) decreases with increasing pH. Hexadecane, as most long chained alkanes, is sparingly soluble in water. The aromatic hydrocarbon 1,3,5 trimethylbenzene (mesitylene) is more soluble than heavier alkanes (solubility: 20 mg/L in water) and less volatile (b.p.: 165°C) than lower molecular weight alkylbenzenes such as toluene or xylene. An aqueous injection can be easily analyzed for by GC-FID with a short retention time. This is an important consideration when a large number of samples must be processed. Therefore, 1,3,5 trimethylbenzene was chosen to test the six PACs.

An initial concentration of 10 mg/L was selected because it is the lowest concentration which can be used to achieve residual concentrations (after adsorption) above the limit of determination (0.1 mg/L x 5) of the GC-FID by direct aqueous injection. This limit could be reduced to 5 to 10 μg/L by using a liquid-liquid extraction procedure to concentrate the samples. However, it would only bring the minimum initial concentration down to 5 mg/L (calculated with: PAC dosage: 75 mg/L, K=0.17, 1/n=0.19). Analysis by direct aqueous injection on a capillary GC was retained as the most practical method, particularly to determine the concentration of a large number of samples.

It was also decided to compare the carbons for their adsorption of phenol, as measured by the modified phenol value test. Phenol compounds are present in the raw water as isomers of ethylphenol and methylphenol. To learn if the initial solute concentration has an important effect on the grading or adsorption behaviour of the PACs, the modified phenol test was also run at a lower initial concentration of 10 mg/L. This would also serve the purpose of comparing directly the adsorption of phenol and the adsorption of mesitylene, and indirectly, the adsorption of mesitylene with the standard modified phenol value test. Adsorption of phenol in river water was measured to obtain an indication of the effect of a complex background matrix on the adsorption of phenol by various PACs. An experiment to compare the adsorption capacity of PACs for mesitylene in river water could not be performed because it was not possible to make direct aqueous injections of river water unto the capillary column.

Finally, adsorption isotherm tests using river water only were performed to test the PACs for their capacity to adsorb humic substances.

3.4.2 Modified Phenol Value Test

Methods for this test are presented in the AWWA B600-78 Standard. A simple procedure was followed, described below.

One litre sodium phosphate dibasic stock buffer (0.73M) was prepared and the pH adjusted to 6.5 with phosphoric acid. From this stock buffer, a single-strength buffer solution (12.5% by volume) was made-up. The 200 mg/L test phenol solution was prepared from a 1000 mg/L stock phenol solution (Fisher,Laboratory grade) in deionized water and the single-strength buffer.

Approximately 1.5 g of each of the six selected PACs was dried at 140°C for three hours or more and cooled in a dessicator. Five dosages of each PAC, 1.5 to 3.5 g/L, were weighed directly in 160 mL septum bottles, which were then covered until fill-up.

A 100 mL aliquot of the test phenol solution was pipetted in each of the five bottles containing carbon and into an empty bottle (blank). The bottles were sealed with Teflon-lined septa and crimped-on aluminum caps.

The bottles were mixed in a custom-built rotary tumbler at 250 rpm for 30 minutes in a temperature controlled room (20°C). Their content was then gravity filtered through a glass microfiber filter (Whatman GF-934 AH, 1.5μm, 150 mm diam.), discarding the first 25 mL, and storing the filtrate in 250 mL glass screw-cap bottles.

The residual phenol concentration was determined by measuring the absorbance at 270 nm with a Pye-Unicam UV-Visible spectrophotometer (SP8-400). The instrument was zeroed with a buffer solution (10% by volume of the stock buffer) made-up for the preparation of standards. The calibration curve, covering the concentration range 20 to 200 mg/L, is included in Appendix 3.

3.4.3 Phenol Adsorption Isotherms

The procedure for the phenol isotherms at low initial concentration was similar to the modified phenol value test method. However, modifications were required, considering the relative importance of losses and the rate of adsorption in this concentration range.

Two sets of experiments were conducted: phenol adsorption isotherms in deionized water, and phenol isotherms in river water. The river water was taken from the raw water intake at the Rossdale Water Treatment Plant on February 27, 1987. The total organic carbon content (TOC) of the filtered river water was 1.8 mg/L, the inorganic carbon content (IC) was 29 mg/L.

Adsorption of Phenol in Deionized Water

Approximately 2.5 g of each PAC sample was dried at 105°C overnight and cooled in a dessicator. Carbon dosages of 25 to 500 mg/L were chosen, based on the expected adsorption of phenol (Dobbs and Cohen, 1980), to result in a residual concentration range of 0.5 to 10 mg/L. These seven carbon dosages were weighed directly into 160 ml dry septum bottles.

A potassium phosphate dibasic (K_2HPO_4; Fisher,Certified ACS) stock buffer solution (0.73M), pH adjusted to 6.5 with phosphoric acid, was made-up. From this stock buffer, single-strength (12.5% by volume) and standard (10% by volume) buffer solutions were prepared. 100 mL of 1000 mg/L stock phenol solution in deionized water was pipetted in approximately 10 L single-strength buffer solution, contained in a 20 L graduated glass carboy. The content was mixed on a large stirring plate (Thermix Stirring Hot Plate Model 610T).

The septum bottles were filled with no headspace by pumping the test phenol solution through carefully rinsed Tygon tubing (class VI, S-50-HL). The bottle fill-up set-up is shown in Figure 3.1. As the bottles were filled, the carbon was wetted by swirling around the first mLs of solution.

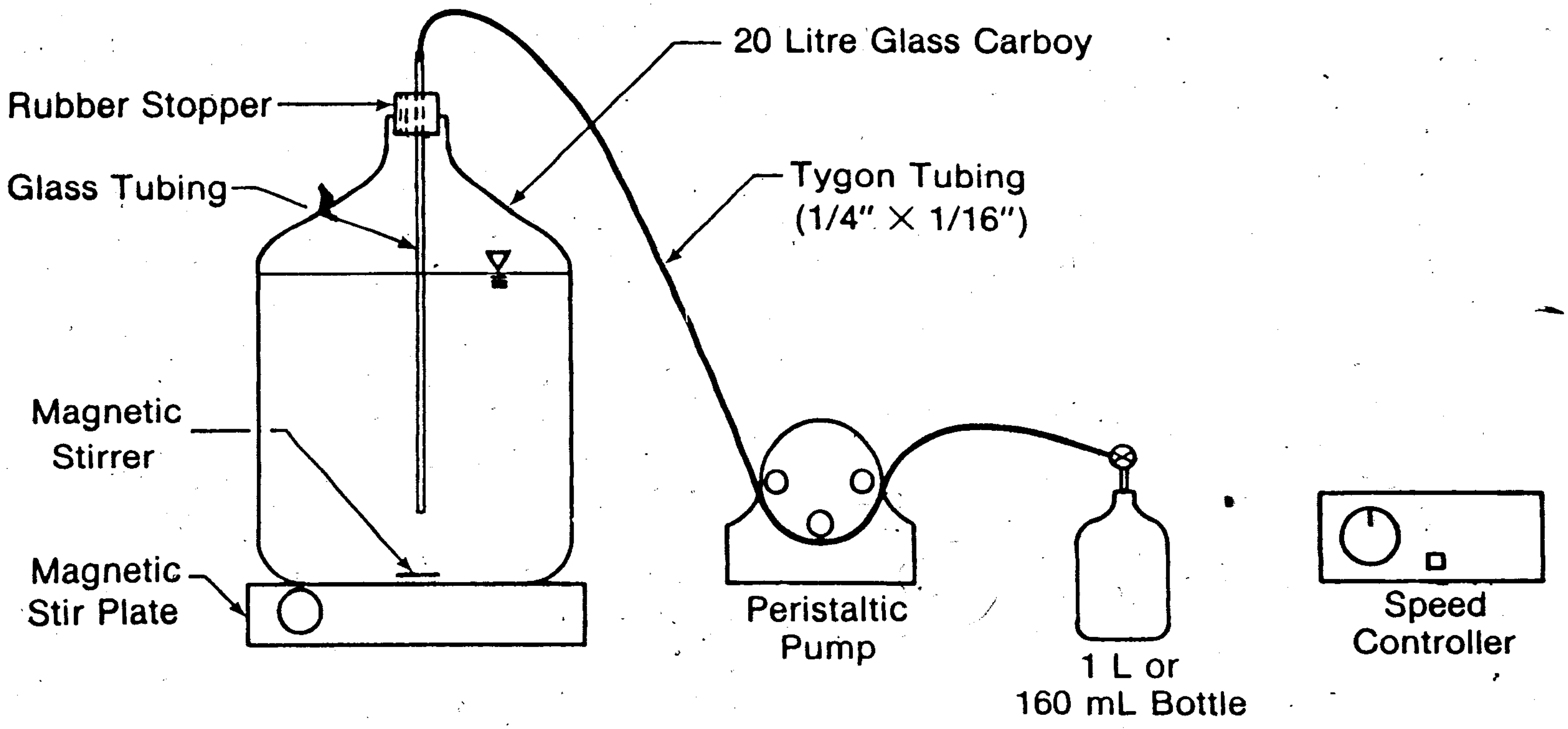

Figure 3.1 Bottle fill-up set-up

Overflow of the carbon/solution mixture was carefully avoided to prevent carbon loss. The batch of phenol solution was mixed continuously during bottle fill-up. Ten litres of solution was sufficient to fill each of the eight bottles for the six PACs tested. Seven bottles contained carbon and one bottle was left blank (test solution only).

The bottles were sealed with Teflon-lined septa and crimped-on aluminum caps. They were then placed in a rotary tumbler at 20°C and mixed at 25 rpm for 5.7 days. A longer mixing time was selected to ensure that a state of equilibrium was reached between the carbon and the phenol in solution.

After mixing, the content of the bottles was immediately centrifuged. Glass centrifuge tubes (50 mL) were filled with no headspace and centrifuged for 15 minutes (setting 5 on an IEC Centrifuge model CL).

The supernatant was analyzed by a 2 μL direct aqueous injection into a gas chromatograph with a flame ionization detector (Hewlett-Packard HP 5730A; 1% SP-1000 on Carbopack B glass column). The temperature of the oven was maintained at 195°C; the detector and injector temperatures were set at 250°C. The gas flows were: hydrogen, 30 mL/min; nitrogen, 20 mL/min; air, 240 mL/min. The concentration of the samples was measured in duplicate and the average used for analysis.

A complete set of isotherm data (six PACs) was analyzed at once. The GC was calibrated beforehand, over the range 0.5 to 10 mg/L, using standards prepared with the stock phenol solution and the standard buffer solution. The standards were analyzed in duplicate or triplicate. The calibration curve is presented in Appendix 3.

Adsorption of Phenol in River Water

This set of adsorption experiments was run similarly to the phenol adsorption isotherms in deionized water.

Using dried as-received carbon, seven dosages, 25 to 500 mg/L, were weighed directly into the septum bottles.

The raw water was slowly pumped through an in-line glass micro fiber filter (Whatman GF/C, 1.2 µm, 42.5 mm diam.) to remove the suspended solids. It was next filtered through a cellulose nitrate membrane filter (MFS, type WCN, 0.45 µm, 47 mm diam.) to remove smaller particles, particularly bacteria, and stored into glass carboys at 5°C.

A 100 mL aliquot of 1000 mg/L stock phenol solution was pipetted in approximately 10 L of filtered river water, previously brought to room temperature. No buffer was added. The solution was mixed on the stirring plate and the bottles filled exactly as for the phenol in deionized water experiment. Mixing, centrifuging and sample analysis were performed as described in subsection "Adsorption of phenol in deionized water".

3.4.4 Mesitylene Adsorption Isotherms

The fraction passing the 325 mesh sieve and retained on the 400 mesh sieve after 10 minutes of shaking on a sieve shaker, was used for this test to eliminate any effect due to particle size. This fraction was washed with deionized water, centrifuged at 2300 rpm for 30 minutes and dried at 105°C for 24 hours. After cooling in a dessicator, it was stored in 40 mL vials with Teflon liners in the dark.

15 L of buffer [illegible] 10 mg/L mesitylene (Fisher Certified) was prepared by adding 150 mL of 1000 mg/L stock mesitylene solution in distilled methanol and 15 mL 1M K_2HPO_4-0.16M KH_2PO_4 stock buffer solution to approximately 15 L deionized water. The pH was adjusted to 8.0 by adding diluted NaOH. A pH of 8.0 was chosen to simulate conditions at the Rossdale Water Treatment Plant. The solution was mixed for 45 minutes on a large stirring plate.

Nine carbon dosages of 5 to 75 mg/L were weighed on aluminum foil pans and poured into 1 L screw-cap bottles with Teflon liners. The dosages were chosen so that a residual concentration range of 0.5 to 10 mg/L would result, by estimating the adsorption for mesitylene. Since adsorption parameters for this compound were not available, the adsorption capacity for p-xylene (K=0.085, 1/n=0.19; Dobbs & Cohen, 1980) was doubled and the resulting parameters used for the estimate (K=0.17, 1/n=0.19).

The test solution was contained in a graduated glass carboy and kept continuously mixed during bottle fill-up. The solution was rapidly pumped in the bottles. Bottles were filled to the top to minimize headspace but carefully avoiding overflow to prevent carbon loss. Twelve bottles were filled for each PAC tested: nine bottles containing the carbon dosages and three blanks, taken at regular interval (1st liter, 7th liter, 12th liter).

The bottles were sealed with Teflon tape around the caps to minimize losses during mixing. They were then placed in a custom-built rotary tumbler (see Figure A.9 in Appendix 9), located in a refrigerated room (5°C, temperature of the raw water at the Rossdale Water Treatment Plant) and rotated at 25 rpm for a minimum of six days. The tumbler was specially designed to hold 1 L screw-cap bottles. When mixing was completed, the bottles were brought to room temperature overnight or for a minimum of eight hours.

Glass centrifuge tubes (50 mL) were filled with no headspace and the samples centrifuged for 15 minutes (setting 5, IEC centrifuge).

Immediately following centrifugation, 3 μL of the supernatant was injected directly into a GC-FID (HP 5890) for analysis. The GC housed a 30 m fused silica capillary column (DB-1, 0.25 mm). The conditions on the GC were as follows: gas flows: hydrogen, 30 mL/min; nitrogen, 25 mL/min; helium 1.5 mL/min and air, 325 mL/min. A split ratio of approximately 7:1 was maintained. The temperature program was: 3 minute hold at 35°C, 5°C/min temperature increase to 65°C and 20°C/min increase to 75°C to remove all water.

A calibration curve was prepared over the concentration range 0.2 to 11.0 mg/L to verify the linearity of the detector's response (see Appendix 3). Aqueous standards were made-up from a standard stock solution of 1100 mg/L mesitylene in triply distilled methanol. The stock solution's concentration was limited by the insolubility of mesitylene. Each day of analysis, the calibration was repeated with two or three freshly prepared aqueous standards, analyzed in duplicate, to adjust the response factor. The aqueous standards could only be used within one hour or less of preparation time due to volatilization losses.

The testing procedure described was checked to determine if significant losses occured. The sequence of verification steps and their results are explained in Appendix 4.

3.4.5 TOC Adsorption Isotherms

The washed and dried carbon fraction passing the 325 mesh sieve but retained on the 400 mesh sieve, of each of the six PACs was used in this experiment. Nine carbon dosages, 15 to 1000 mg/L, were weighed on aluminum foil pans and poured into 1 L screw-cap bottles.

River water taken at the raw water intake of Rossdale Water Treatment Plant on March 8, 1986, during spring runoff, served as the testing solution. Approximately 80 L were transferred into a 100 L polyethylene cylindrical container. A polyethylene paddle (190 mm x 100 mm) attached to a stainless steel rod was placed in the container. A stirrer rotated it at 100 rpm to keep the water completely mixed. No buffer solution was added to the water.

A pump recirculated the water continuously through Tygon tubing. To fill up a bottle, a three-way valve was opened, momentarily interrupting water circulation. The bottles were filled to the rim, taking care to avoid losses of carbon by overflow. For each PAC, the first bottle filled was a blank, i.e., contained river water only, then nine bottles containing the preweighed carbon dosages were filled. All 60 bottles were placed in a rotary tumbler at 5°C and mixed at 25 rpm for six days.

After mixing, the content of the bottles was settled for two hours then gravity filtered through glass micro fi- [illegible] (Whatman GF-934 AH). The filtrate was collected into 15 [illegible] Teflon-lined vials and stored at 5°C until analysis.

The total organic content (TOC) of the samples was measured using a Dohrmann DC-80 Carbon Analyzer equipped with a Horiba PIR-200 Infrared Gas Analyzer. The TOC was calculated from the difference between the total carbon (TC) and the inorganic carbon (IC). Each sample was analyzed in duplicate. The instrument was calibrated by repeated 1 mL injections of 10 mg/L potassium hydrogen phthalate.

4. RESULTS

4.1 Adsorption Isotherms

Most of the results from the screening and testing of the PACs are plotted as adsorption isotherms. An isotherm is a graph of the distribution of the solute between the liquid phase (solution) and the solid phase (activated carbon), at equilibrium and at a constant temperature. It represents the relationship between the carbon loading and the equilibrium concentration. The loading achieved on a particular carbon is the amount of solute adsorbed per unit mass carbon, or the concentration of solute adsorbed per carbon dosage. The solute concentration remaining in solution at the end of an adsorption isotherm experiment is termed the equilibrium concentration if it is thought, with confidence, that a state of dynamic equilibrium has been reached in the adsorption process. The more general expression, residual concentration, is used when the contact time between the activated carbon and the solution is shorter than would be thought necessary to reach equilibrium.

Although two classical models exist for fitting adsorption isotherm data: the Freundlich and Langmuir equations, the Freundlich model is more commonly used for water treatment applications and was used to fit the data in this study. The Freundlich or van Bemmelen equation states that the adsorptive capacity of an adsorbent is a function, although not directly, of the equilibrium concentration (see Table 4.1). It is based on the assumptions that only a single layer of solute can be adsorbed on the surface of the adsorbent and that no transmigration of the adsorbate occurs in the plane of the surface. The Freundlich equation is a special case of the Langmuir equation where the constant K takes into account the heterogeneous surface energies ($K \propto RTnbe^{\Delta H/RT}$, where b is a Langmuir constant related to the net energy of adsorption). Although the basic assumptions used to derive the equation are seldom met in water treatment, the equation offers a good means of representing the adsorption equilibrium (Weber, 1972).

For plotting, the equation is linearized by taking the logarithm of both sides of the equation. The constants K and 1/n are designated as the Freundlich parameters and estimated from the regression line fitted to the data. K has been used as an indicator of the adsorption capacity of a carbon for a given compound and 1/n as an indicator of the adsorption intensity or the effect of concentration on capacity.

Table 4.1 Freundlich equation

$$q_e = K\ C_e^{1/n}$$

$$\text{where: } q_e = \frac{C_0 - C_e}{M}$$

where: C_0: initial solute concentration

C_e: equilibrium solute concentration

M: carbon dosage

q_e: carbon loading

K, 1/n: constants, Freundlich parameters

Linearized form:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

where: log K: ordinate intercept

1/n: slope

4.2 Screening Results

4.2.1 Particle Size Analysis

Ten PAC samples were sieved to determine their particle size distribution. Due to the small sample provided by the manufacturer, the carbon Norit W-20 was not analyzed. For each activated carbon, the percent mass passing the consecutive sieves of mesh size 100, 200 and 325 and the total losses are compiled in Table 4.2.

Losses ranged between 0.2 and 3.3%. Most losses were incurred by leaks between the sieves during the sieve shaking.

Only five PAC samples satisfied the particle size distribution recommended by AWWA. However, Aqua Nuchar's particle size distribution could be considered satisfactory since the percent fraction passing the 325 sieve is only 2.6% lower than 90% and 2.3% carbon was lost during the procedure. The size distribution of PACs Watercarb Plus, Darco S-51, Pac 20B and WTC suggest slightly coarser carbons.

The water content of the PAC samples ranged from 0.7 to 10%. Only the Westvaco carbons, Aqua Nuchar and Aqua Pac did not meet the recommended maximum moisture content of 8%.

Table 4.2 Particle size distribution and moisture content

PAC	Particle size analysis				Moisture Content (%)
	(Percent passing sieve no.)			Loss (%)	
	100	200	325		
[illegible]a Nuchar	100	99.7	87.6	2.3	10
[illegible]ua Pac	100	99.9	91.4	1.5	10
WPH	100	99.9	94.1	0.6	4.8
WPL	100	99.9	95.2	3.1	1.8
Watercarb	99.4	97.2	92.0	1.2	4.0
Watercarb Plus	99.4	96.7	72.4	0.2	0.96
Darco S-51	99.1	83.9	56.8	3.0	5.7
Hydrodarco B	100	99.5	90.1	1.4	6.3
Pac 20B	92.8	76.0	56.0	0.8	4.3
WTC	87.1	77.5	63.9	3.3	0.68
AWWA Standard	99	95	90		8

4.2.2 Iodine Number Test

All PAC samples were tested in triplicate for their iodine number. The average iodine number and its 95% confidence interval, based on the standard deviation of the replicates, are compiled in Table 4.3. The confidence limits for the carbons Aqua Pac and WTC were calculated using the mean variance of all the results. This was done because, of the three replicate titrations, only one resulted in a residual filtrate normality within the limits required to apply an appropriate correction factor. In Figure 4.1, the carbons are graded in order of decreasing iodine number. The lines represent the 95% confidence interval in which the iodine number lies. As a reference, the AWWA recommended minimum of 500 mg/g is shown.

Iodine numbers ranged from 385 to 875 mg/g. The Norit carbons (Darco S-51, Norit W-20 and Hydrodarco B) show the lowest adsorption capacity for iodine. The two grades of PACs manufactured by Calgon (WPH and WPL) have almost identical iodine numbers. It is also interesting to note that WTC, the PAC used at the Edmonton Water Treatment Plants in previous years, displays the lowest iodine number, much below the AWWA recommended minimum value.

4.2.3 Tannin Value Test

The tannic acid isotherm data was fitted to the Freundlich model using a linear regression analysis, from which

Table 4.3 Iodine number

PAC	Iodine number (mg/g)	95% confidence limits
Aqua Nuchar	842	(833, 851)
Aqua Pac	634	(623, 645)
WPH	770	(759, 781)
WPL	780	(776, 784)
Watercarb	625	(606, 644)
Watercarb Plus	675	(668, 682)
Darco S-51	579	(564, 594)
Hydrodarco B	460	(451, 469)
Norit W-20	526	(518, 534)
PAC 20B	875	(822, 928)
WTC	385	(374, 396)

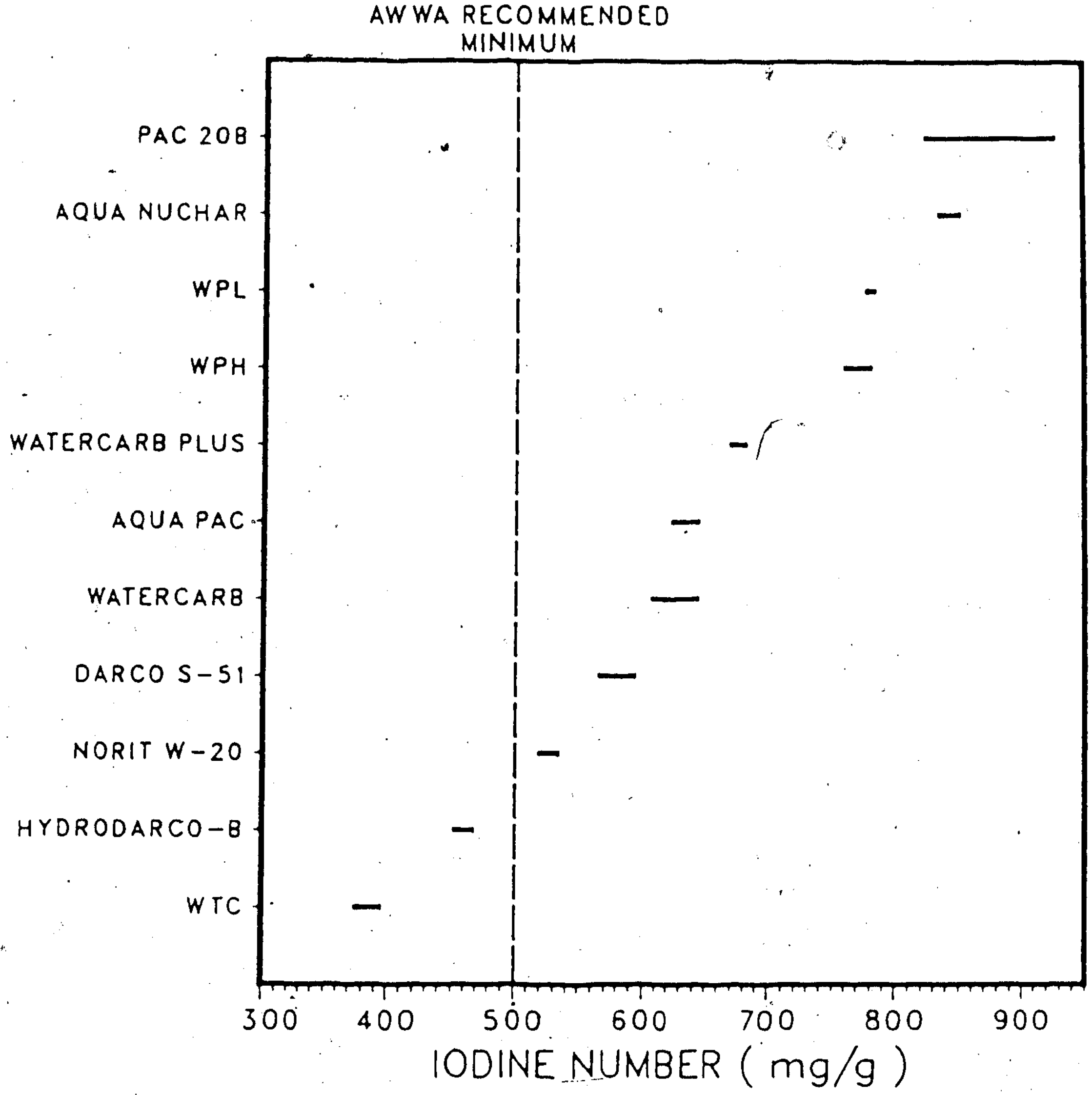

Figure 4.1 Iodine number and 95% confidence interval

the constants K and 1/n were estimated. These parameters, their 95% confidence interval, as well as a regression coefficient (R^2), are tabulated for each carbon in Table 4.4. Ranges of carbon dosages varied for each carbon, depending on the expected tannin value. All carbons were initially tested with a dosage range of 50 to 400 mg/L (Figure 4.2). For the PACs for which a 400 mg/L dosage was insufficient to achieve the 2 mg/L tannic acid residual concentration, an additional isotherm test was run with higher carbon dosages (Figure 4.3). To determine the tannin value, the carbon loading at a residual concentration of 2 mg/L was predicted from the regression line. The calculated tannin values, with their 95% prediction interval, are compiled in Table 4.5.

In general, it can be noted that these PACs, designed for water treatment, do not adsorb tannic acid well. The adsorption capacity (as measured at 1 mg/L residual concentration) ranges from 0.01 to 0.05 mg tannic acid adsorbed per mg carbon. Or stated differently, 275 mg/L of the best PAC for tannic acid adsorption (Darco S-51) was required to remove 90% of tannic acid in solution. With 50 mg/L, the most tannic acid adsorbed was 29%. The preliminary tannin value tests show a wide difference in extent of adsorption of tannic acid with identical dosages of PAC. A dosage of 400 mg/L WTC adsorbed 44.5% of a 20 mg/L tannic acid solution while the same dosage of Darco S-51 adsorbed 96.8%. The carbons Hydrodarco B, Darco S-51 and Aqua Nuchar which can

Table 4.4 Tannin value test isotherm results

PAC	Isotherm parameters				R^2
	K (mg/mg)	95% confidence interval	1/n	95% confidence interval	
Aqua Nuchar	0.0521	(0.0501,0.0550)	0.254	(0.226,0.282)	0.997
Aqua Pac	0.0117	(0.0089,0.0155)	0.224	(0.076,0.372)	0.886
WPH	0.0302	(0.0269,0.0339)	0.204	(0.138,0.270)	0.970
WPL	0.0319	(0.0275,0.0363)	0.168	(0.091,0.245)	0.942
Watercarb	0.0149	(0.0115,0.0191)	0.184	(0.028,0.340)	0.825
Watercarb Plus	0.0219	(0.0182,0.0263)	0.106	(0.019,0.193)	0.833
Darco S-51	0.0565	(0.0501,0.0631)	0.236	(0.173,0.299)	0.979
Hydrodarco B	0.0440	(0.0295,0.0646)	0.396	(0.160,0.632)	0.904
Norit W-20	0.0179	(0.0129,0.0245)	0.238	(0.064,0.412)	0.864
WTC	0.0126	(0.0107,0.0148)	0.235	(0.147,0.323)	0.960
PAC 20B	0.0161	(0.0069,0.0380)	0.055	(-0.322,0.432)	0.067

Table 4.5 Tannin value

PAC	Range of dosages (mg/L)	Tannin value (mg/L)	95% prediction interval
Aqua Nuchar	50-400	290	(271,311)
Aqua Pac	250-1500	1280	(929,1770)
WPH	100-500	508	(442,583)
WPL	100-500	488	(415,573)
Watercarb	250-1500	1060	(700,1600)
Watercarb Plus	100-750	776	(617,977)
Darco S-51	50-400	275	(229,331)
Hydrodarco B	50-400	316	(186,537)
Norit W-20	100-1000	842	(557,1280)
WTC	250-1250	1190	(990,1430)
PAC 20B	100-1000	1070	(502,2290)

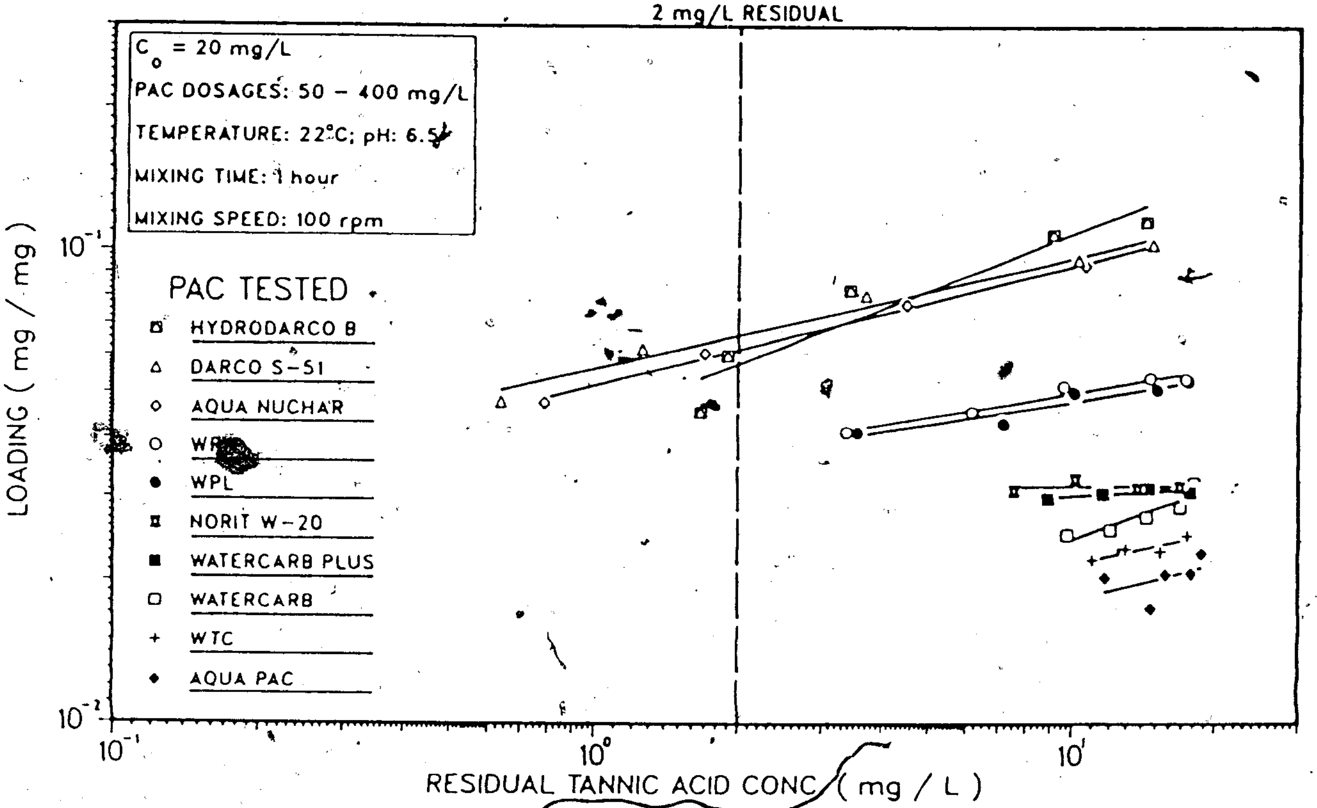

Figure 4.2 Tannin value test - Initial isotherms

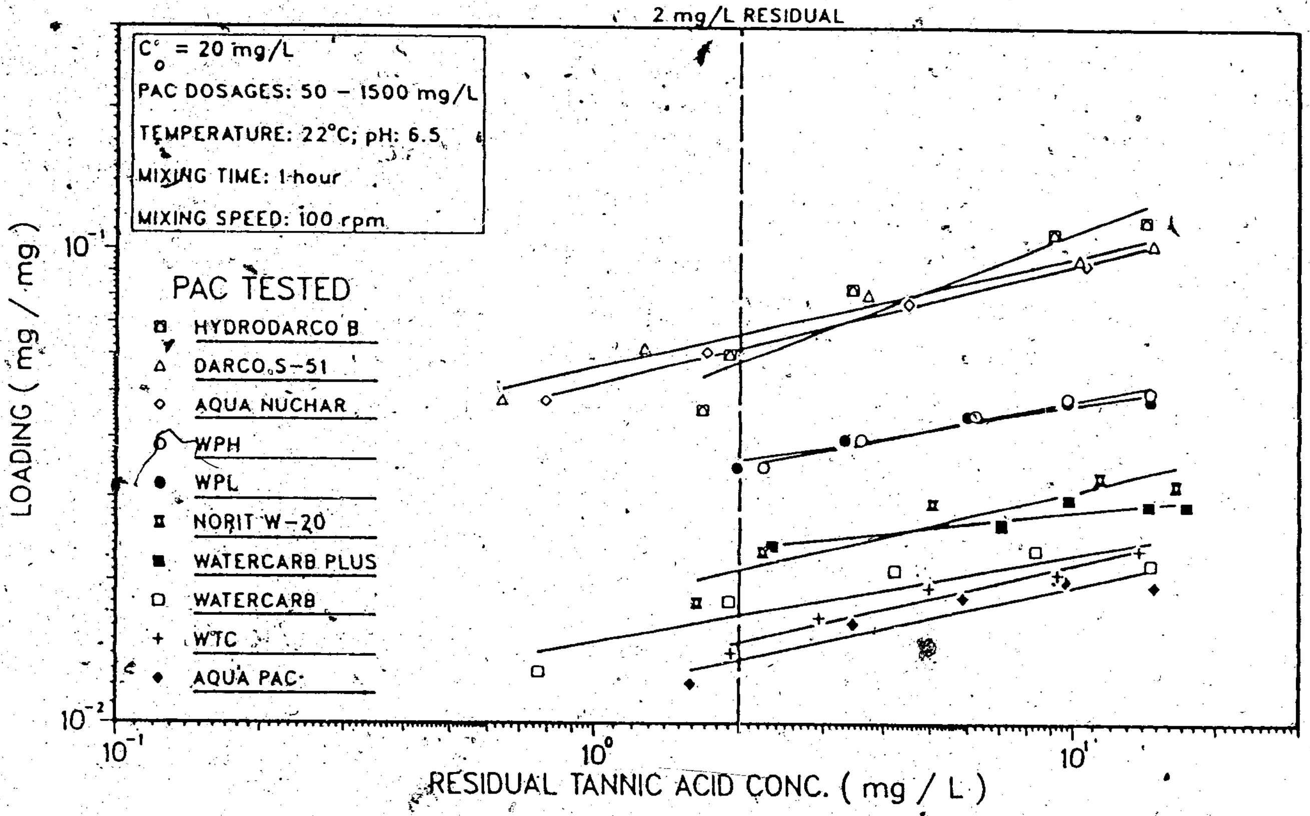

Figure 4.3 Tannin value test - Final isotherms

be considered equivalent, exhibit the most capacity for tannic acid. The carbon WPL has the same adsorption capacity as the higher grade WPH. A grading of the five other PACs cannot be distinguished since the difference in their adsorption capacity for tannic acid is not significant (95% confidence level). The results from the isotherm tests with the carbon Pac 20B did not fit the Freundlich equation.

4.2.4 Selection of PACs for Further Testing

From the results of the particle size analysis, iodine number and tannin value tests, six PACs were to be chosen for further isotherm experiments. These results are summarized in Table 4.6. From the eleven PACs, three were readily eliminated, as justified below.

1- WTC (Transpacific Carbon). Although it was the carbon used at the City of Edmonton's Water Treatment Plants, its characteristics were much lower than could be obtained from the other available PACs. That is: an iodine number much lower than the AWWA Standard; a very high tannin value; an inadequate particle size distribution.

2- Norit W-20 (Norit). This PAC was eliminated mainly because: it is manufactured in the Netherlands and a small, insufficient sample was shipped for testing; its iodine number is very low; at low dosages (50 mg/L), very low loadings of tannic acid were achieved.

3- Pac 20B (Cecarbon). Although it adsorbs iodine very well as shown by its iodine number, it was eliminated because: it

Table 4.6 Summary of screening results

PAC	Paticle size distr. (percent passing #)			Iodine number		Tannin value	
	100	200	325	(mg/g)	grading	(mg/L)	grading
Pac 20B	92.8	76.0	56.0	875	1	1070	9
Aqua Nuchar	100	99.7	87.6	842	2	290	2
WPL	100	99.9	95.2	780	3	488	4
WPH	100	99.9	94.1	770	4	508	5
Watercarb Plus	99.4	96.7	72.4	675	5	776	6
Aqua Pac	100	99.9	91.4	634	6	1280	11
Watercarb	99.4	97.2	92.0	625	7	1060	8
Darco S-51	99.1	83.9	56.8	579	8	275	1
Norit W-20				526	9	842	7
Hydrodarco B	100	99.5	90.1	460	10	316	3
WTC	87.1	77.5	63.9	385	11	1190	10

adsorbs very little tannic acid; it contains a higher fraction of larger particles than is considered acceptable by the AWWA Standard.

The best adsorption of small compounds, as tentatively characterized by the iodine number, was achieved with Aqua Nuchar. The best adsorption of larger compounds, here measured by the tannin value test, was obtained with Darco S-51. These carbons were thus chosen for further analysis. The two Calgon PACs, WPH and WPL, have very similar characteristics according to these three tests. Instead of choosing one or the other, it was decided to test both to compare their cost-effectiveness. Two more PACs were then eliminated for the following reasons.

4- Watercarb Plus (Husky). Comparison of the Husky PACs, Watercarb and Watercarb Plus, indicated that while they adsorb iodine equally, Watercarb Plus has an unsatisfactory particle size distribution and, at low dosages (50 mg/L), it adsorbs less tannic acid than Watercarb.

5- Aqua Pac (Westvaco). Of the two PACs remaining, Hydrodarco B and Aqua Pac, the latter was eliminated because: it adsorbs tannic acid poorly; it has an average iodine number while Hydrodarco B would be a PAC representative of low iodine number.

In summary, the carbons Aqua Nuchar, WPH, WPL, Watercarb, Darco S-51 and Hydrodarco B were chosen to be tested further. They are representative of a wide range of available iodine numbers (460 to 842 mg/g) and tannin values (275 to 1070 mg/L). One has a below-standard iodine number (Hydrodarco B); one PAC has a high tannin value (Watercarb); one carbon does not satisfy the standard for particle size distribution (Darco S-51).

4.3 Testing Results

4.3.1 Modified Phenol Value Test

The phenol adsorption isotherms performed to determine the modified phenol value are shown in Figure 4.4. The isotherm parameter estimates are compiled in Table 4.7. The carbon loadings were calculated and plotted as [illegible] adsorbed per g/L PAC. However, to permit a comparison of the phenol adsorption capacity with the capacity for other compounds, K values in mg/mg are also included. Similarly to the tannin value test, the modified phenol value is calculated using a loading (at 10% residual concentration) predicted from the regression line of the isotherm (see Table 4.8).

The PACs Watercarb, WPL and WPH adsorbed phenol equally well. The PACs Aqua Nuchar, Darco S-51 and Hydrodarco B, which had shown the most capacity for tannic acid, did not remove phenol to the same extent. The isotherm lines are all nearly parallel (1/n: 0.15 to 0.28), over the range of residual concentrations, indicating that the PACs can be graded

Table 4.7 Modified phenol value iso[illegible]results

PAC	Isotherm parameters					R²
	K (mg/mg)	K (%/g/L)	95% conf. interval	1/n	95% conf. interval	
WPH	0.0438	25.6	(25.1,26.3)	0.223	(0.211,0.235)	0.999
WPL	0.0440	25.8	(24.5,26.9)	0.229	(0.201,0.257)	0.996
Aqua Nuchar	0.0248	15.2	(14.5,15.8)	0.280	(0.262,0.298)	0.999
Watercarb	0.0480	27.6	(24.5,30.9)	0.210	(0.151,0.269)	0.977
Hydrodarco B	0.0298	16[illegible]	(12.6,21.9)	0.151	(0.069,0.233)	0.921
Darco S-51	0.0280	16.3	(15.5,17.0)	0.218	(0.203,0.233)	0.999

Table 4.8 Modified phenol value

PAC	Modified phenol value (g/L)	95% prediction interval
WPH	2.10	(2.06, 2.15)
WPL	2.06	(1.92, 2.21)
Aqua Nuchar	3.11	(3.05, 3.19)
Watercarb	2.01	(1.71, [illegible].37)
Hydrodarco B	3.84	(3.34, 4.41)
Darco S-51	3.34	(3.27, 3.42)
AWWA Standard	max:3.5	

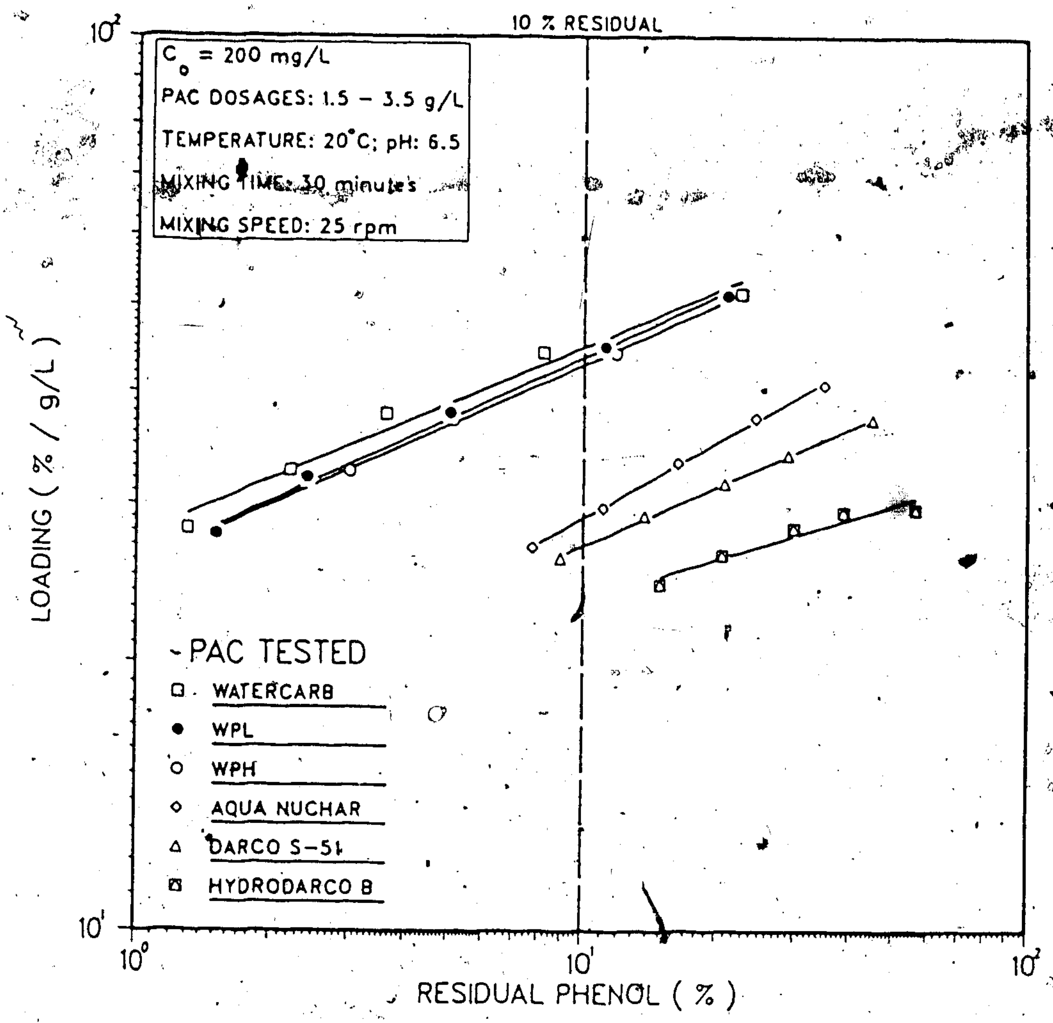

Figure 4.4 Modified phenol value test - isotherms

on the basis of the one point estimate: the modified phenol value.

4.3.2 Phenol Isotherms in Deionized Water

The second set of phenol isotherms were performed with an initial concentration of 7 to 9 mg/L. The grading of the PACs tested was similar to the grading obtained with the modified phenol value test, as shown in Figure 4.5 and in Table 4.9. No significant difference in capacity was measured for the PACs Watercarb, WPH and WPL. These carbons achieved better phenol removals than Aqua Nuchar, Darco S-51 and Hydrodarco B. The PAC Aqua Nuchar presented a very steep slope (0.65), indicating a rapid decrease in capacity with decreasing solute concentrations. The adsorption capacities, measured by K, were similar to the capacity values obtained with the modified phenol value procedure.

4.3.3 Phenol Isotherms in River Water

The phenol in river water isotherms are shown in Figure 4.6. Curvature of the isotherm lines was observed at high solute concentrations, which indicates a lowered adsorption capacity for phenol at low carbon dosages. This is due to the competition, from the dissolved organics in the river water matrix, for the limited number of available adsorption sites.

Table 4.9 Phenol isotherms in deionized water results

PAC	Isotherm parameters					R^2
	K (mg/mg)	K (%/mg/L)	95% conf. interval	1/n	95% conf. interval	
WPH	0.051	0.38	(0.32,0.44)	0.19	(0.14,0.24)	0.97
WPL	0.058	0.44	(0.36,0.54)	0.17	(0.10,0.24)	0.95
Aqua Nuchar	0.021	0.05	(0.01,0.18)	0.65	(0.30,1.0)	0.87
Watercarb	0.055	0.53	(0.40,0.70)	0.13	(0.05,0.22)	0.90
Hydrodarco B	0.026	0.17	(0.11,0.26)	0.25	(0.14,0.36)	0.91
Darco S-51	0.028	0.21	(0.13,0.35)	0.21	(0.08,0.34)	0.83

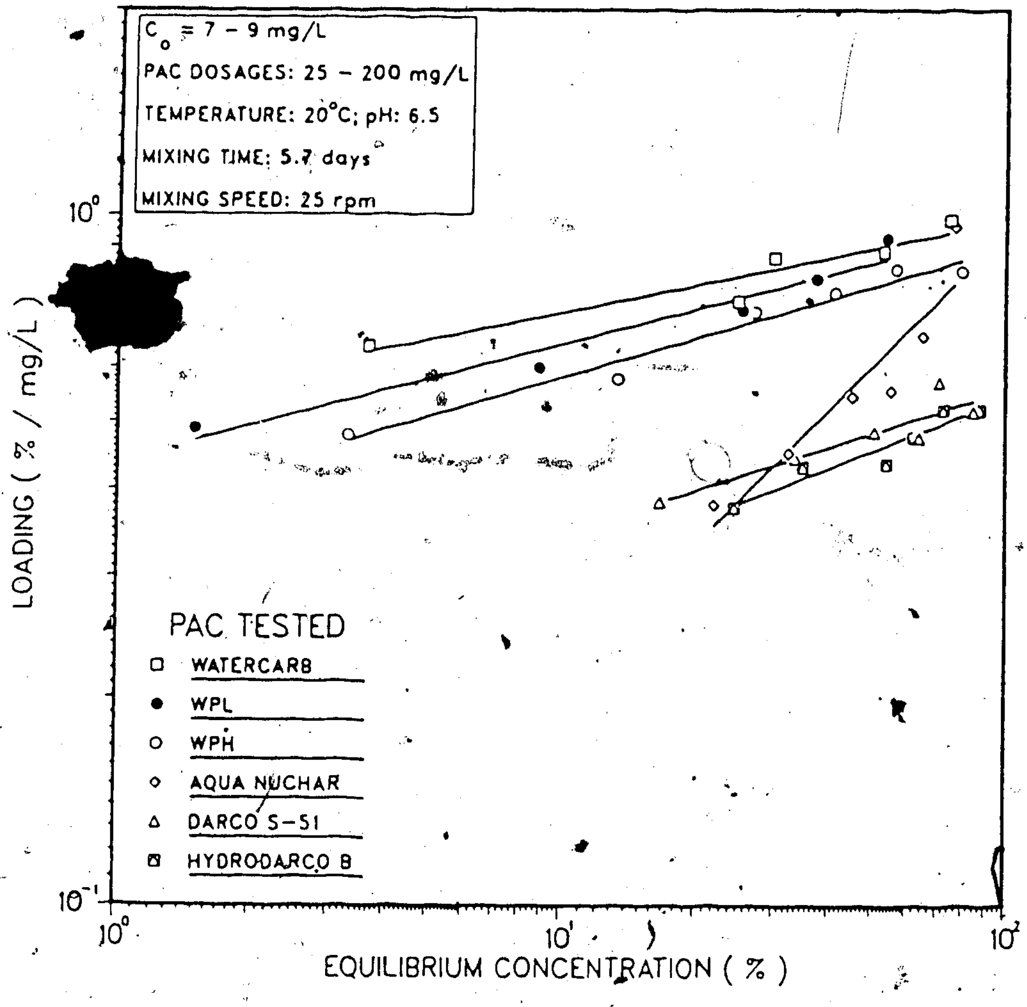

Figure 4.5 Phenol isotherms in deionized water

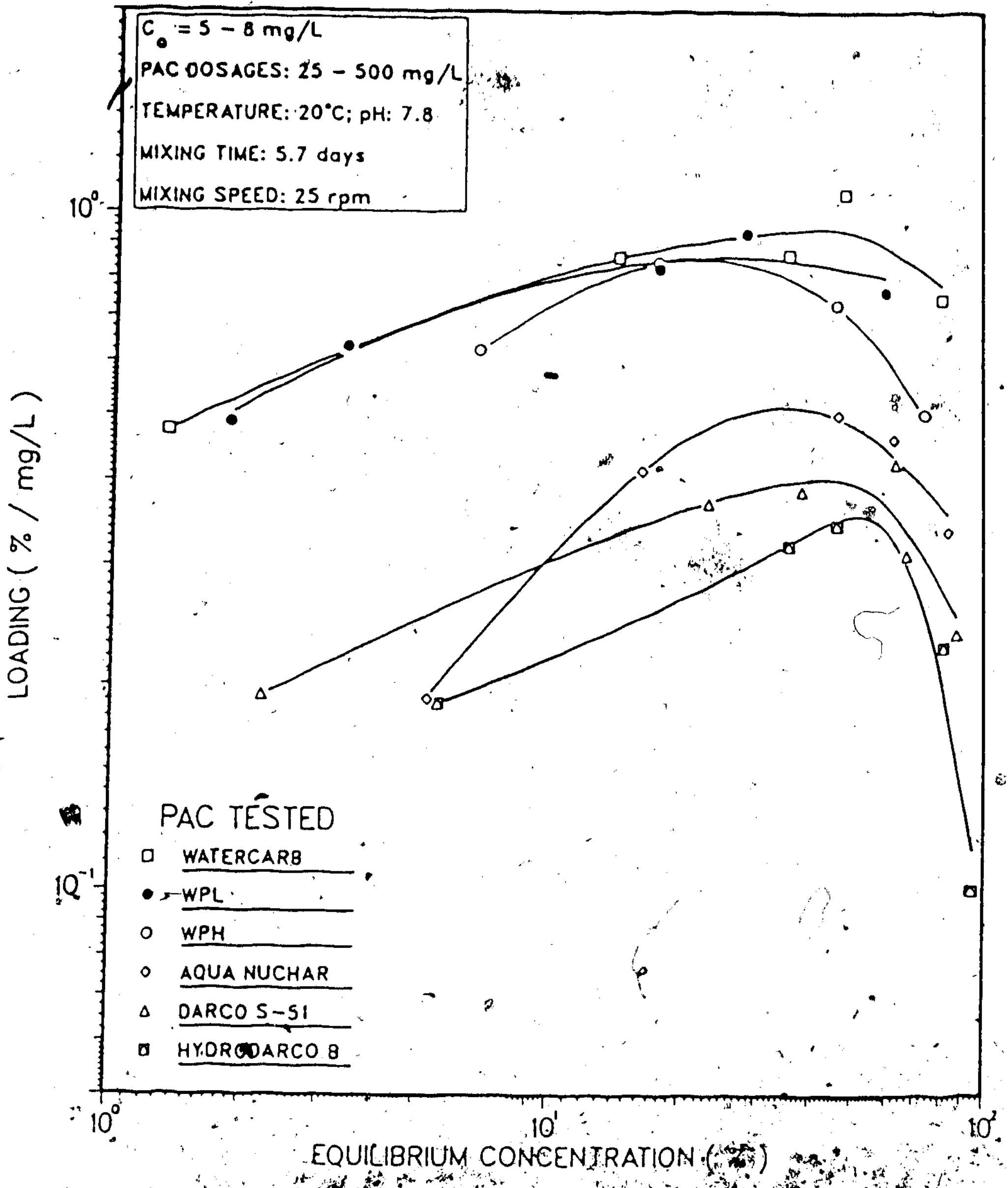

Figure 4.6 Phenol isotherms in river water (N. Saskatchewan River, February 27, 1987)

Although the results were plotted according to the linearized Freundlich equation, the non-linear isotherms could not be characterized by [illegible] Freundlich parameters. A comparison of the PACs was then based on the difference between their carbon loadings at each dosage level. A reference frequency distribution was prepared to determine if differences between adsorption capacities were significant, using a 90% confidence level. In order to draw this distribution, it was assumed that the mean variance of the river water isotherm results was identical to the mean variance of the phenol in deionized water isotherms. The latter was the weighed mean of five deionized water isotherm variances, which were found to be consistent. This assumption was based on the fact that an identical experimental procedure was followed for both tests.

At low PAC dosages, the grading was clearly: Watercarb, WPL, WPH, Aqua Nuchar, Darco S-51 and Hydrodarco B, based on the significant differences (90% level) in their adsorptive capacities. At higher dosages, the same grading as with the modified phenol value test and the phenol in deionized water experiments was obtained, where the PACs Watercarb, WPL and WPH displayed equivalent adsorption capacities for phenol.

The isotherms in both water matrices were superimposed for each PAC tested, as shown in Figures 4.7 to 4.12. A comparison of the isotherms, based on the difference in

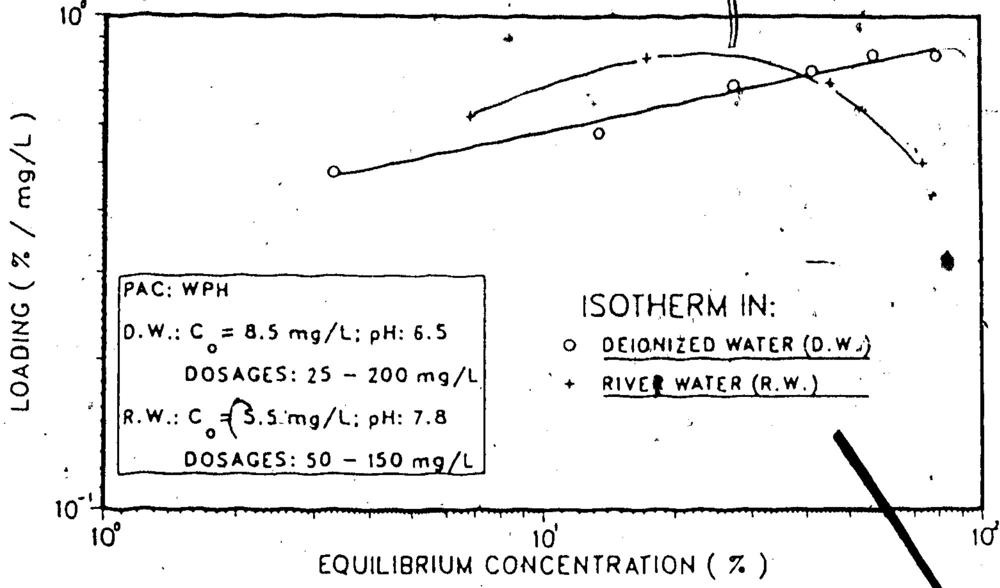

Figure 4.7 WPH - Phenol isotherms

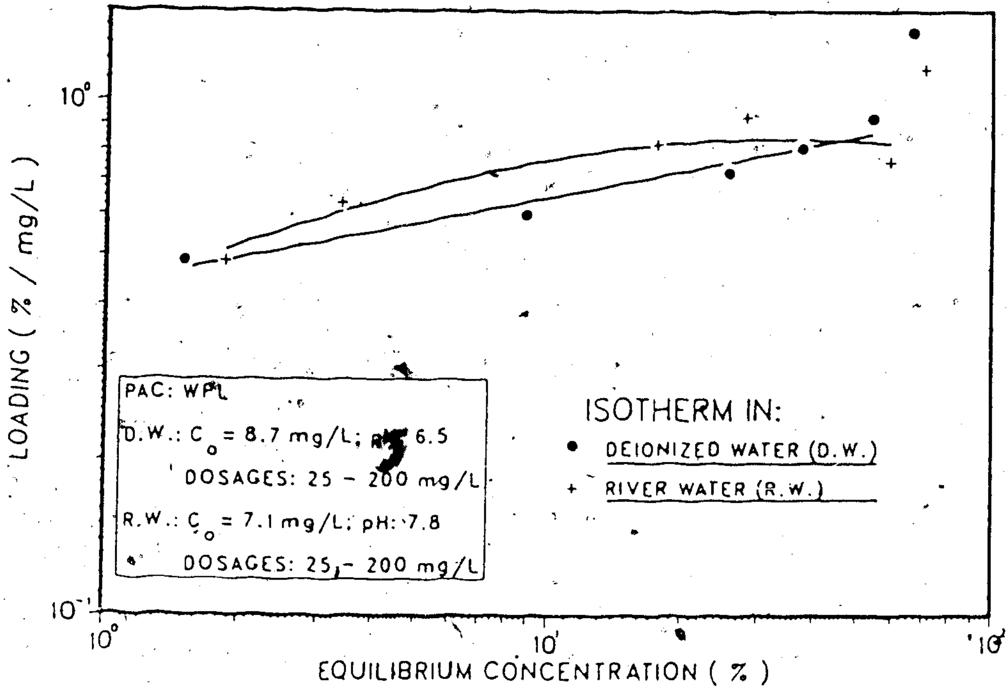

Figure 4.8 WPL - Phenol isotherms

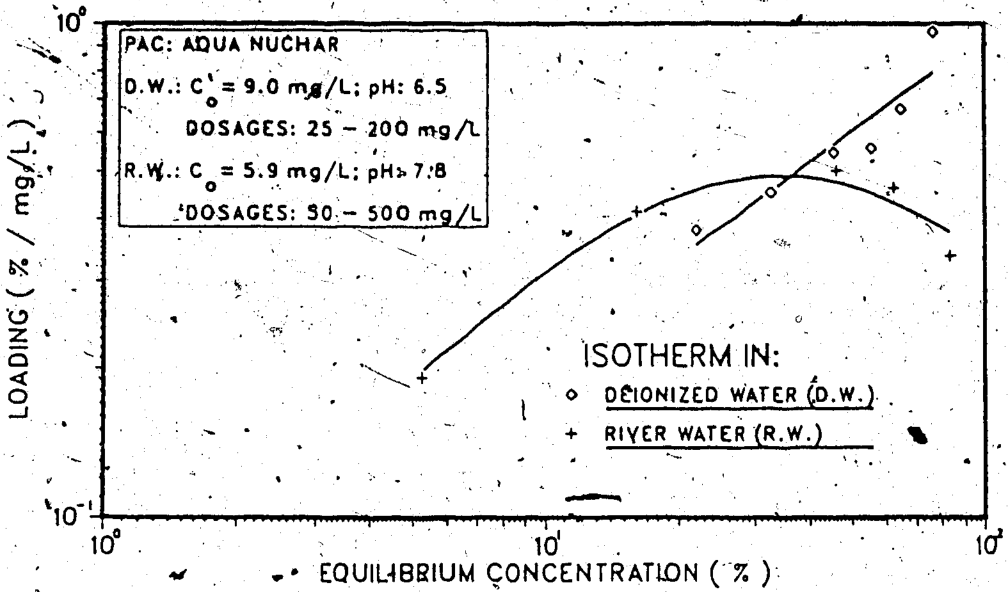

Figure 4.9 Aqua Nuchar - Phenol isotherms

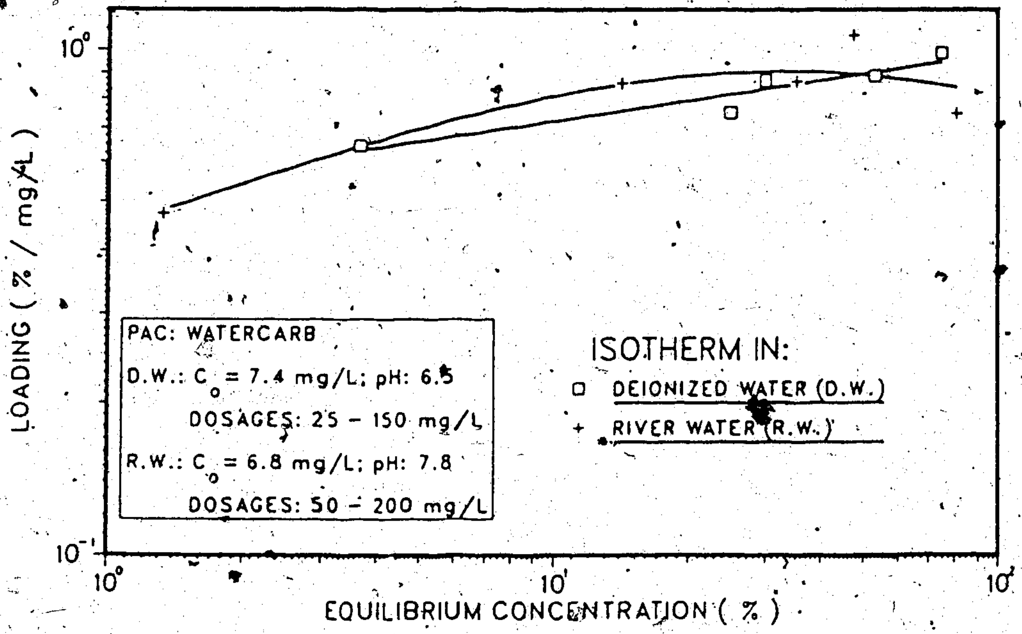

Figure 4.10 Watercarb - Phenol isotherms

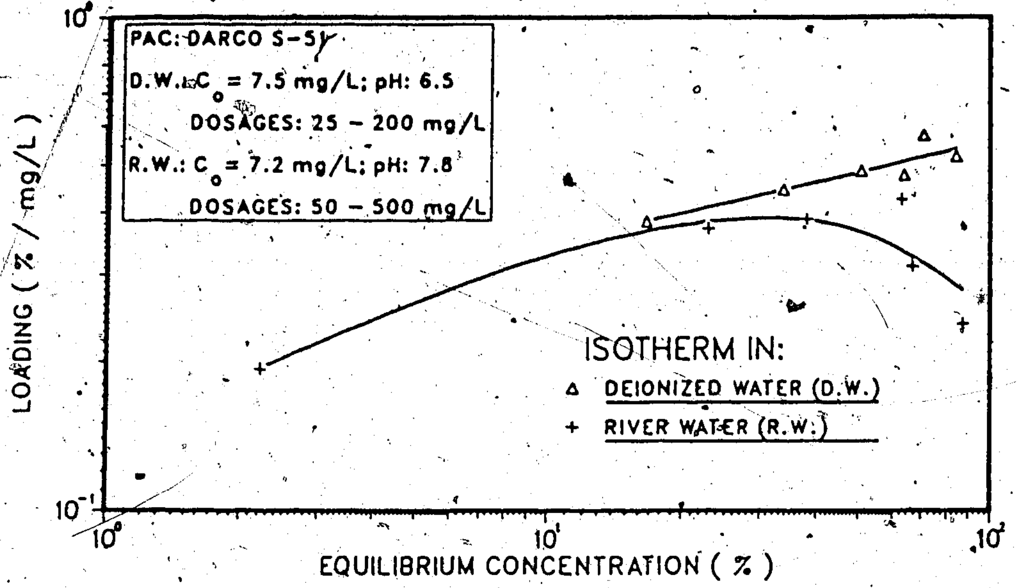

Figure 4.11 Darco S-51 - Phenol isotherms

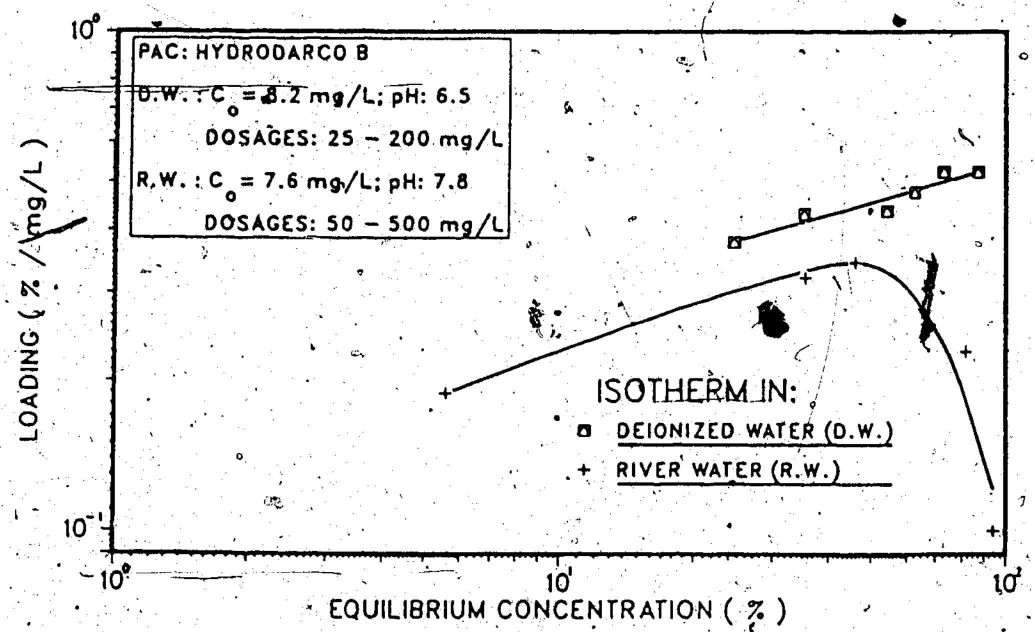

Figure 4.12 Hydrodarco B - Phenol isotherms

loadings at each dosage level, indicated that, for each PAC, the observed decrease in capacity for phenol in river water is significant at low dosages. This reduction in capacity was larger for Aqua Nuchar, Hydrodarco B and Darco S-51, the PACs which displayed a better potential for adsorption of tannic acid. At higher dosages, the competition effect induced a significant decrease in capacity for Hydrodarco B only. Superior phenol removal in river water, observed for four out of six carbons was not confirmed statistically, as the differences between the loadings were not consistently significant. The discrepancy can however be caused by the difference in pH of the test solutions.

4.3.4 Mesitylene Isotherms

Results of the adsorption of mesitylene on the six carbons tested are compiled in Table 4.10 and plotted in Figures 4.13. Measured initial concentrations of mesitylene varied from 7.0 to 9.6 mg/L, therefore normalized isotherms were plotted for direct comparison. Figure 4.13 shows the data points used to calculate the regression line, while all the data points are present in the individual isotherms in Appendix 7.

Mesitylene was found to be more adsorbable than phenol, an expected result due to its lower solubility. Calgon WPL and WPH showed identical capacities for mesitylene. They removed mesitylene much better than the four other carbons,

Table 4.10 Mesitylene isotherms in deionized water results

PAC	Isotherm parameters					R^2
	K (mg/mg)	K (%/mg/L)	95% conf. interval	1/n	95% conf. interval	
WPH	0.16	1.8	(1.4,2.2)	0.095	(0.025,0.17)	0.73
WPL	0.17	1.8	(1.4,2.2)	0.10	(0.030,0.17)	0.71
Aqua Nuchar	0.094	0.33	(0.17,0.62)	0.50	(0.33,0.67)	0.87
Watercarb	0.089	0.33	(0.13,0.83)	0.44	(0.20,0.68)	0.81
Hydrodarco B	0.077	0.39	(0.21,0.72)	0.38	(0.22,0.54)	0.82
Darco S-51	0.094	0.63	(0.48,0.83)	0.24	(0.17,0.31)	0.92

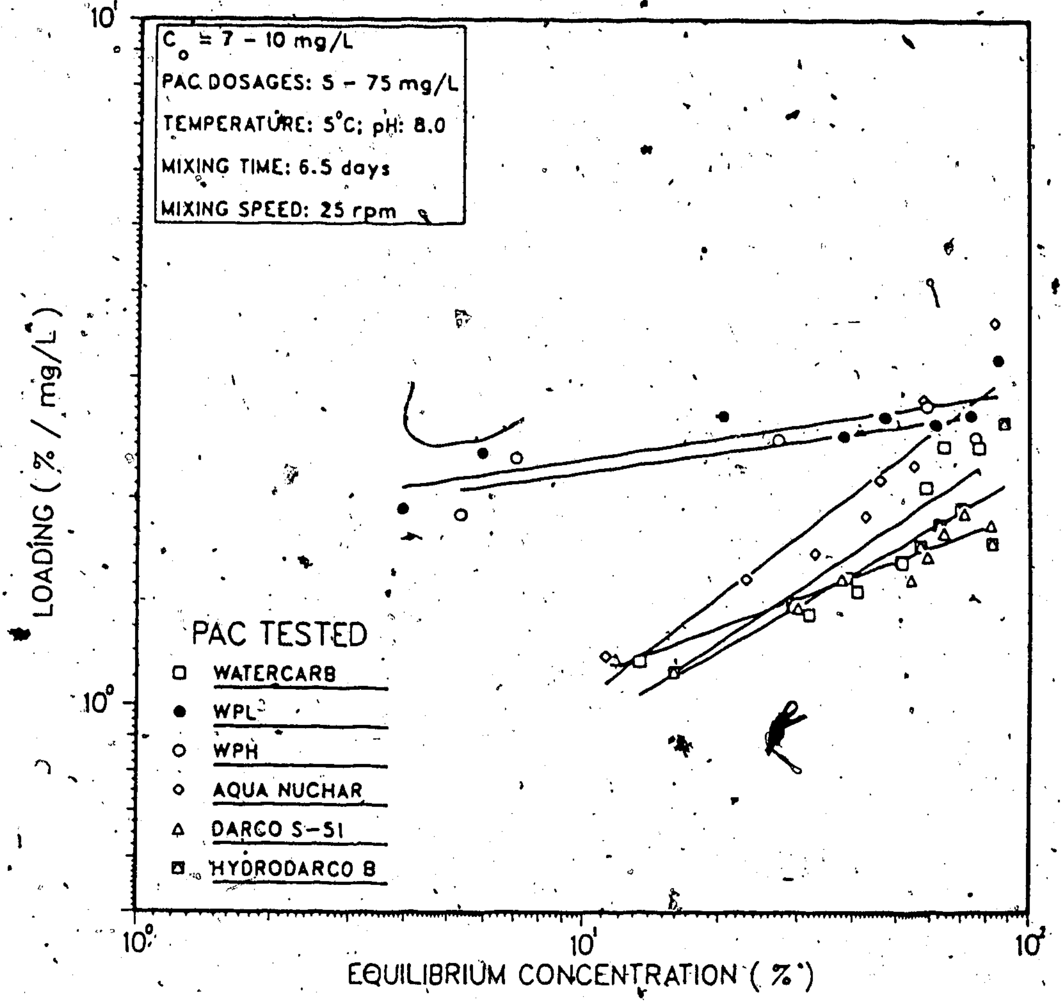

Figure 4.13 Mesitylene isotherms

displaying constantly high carbon loadings. Watercarb which presented the best capacity for phenol, adsorbed mesitylene to the same extent as Aqua Nuchar and the Norit carbons.

4.3.5 TOC Isotherms

The results from the TOC isotherm experiments did not fit the Freundlich, nor the Langmuir, nor a modified Freundlich model which takes into account the non-adsorbable fraction (Kaastrup *et al.*, 1984). However, to illustrate the potential for TOC adsorption, the percent TOC adsorbed versus the dosage is plotted in Figure 4.14.

At low dosages, the carbons Aqua Nuchar and Hydrodarco B adsorbed the most TOC. Again the PACs WPH and WPL displayed very similar adsorption capacity. Watercarb adsorbed TOC the least. These results follow the tannic acid adsorption test results. No more than 46% TOC was removed with PAC dosages of 100 mg/L or less. Dosages of 1000 mg/L were not sufficient to remove all TOC. A non-adsorbable fraction ranging from 4% to 12% of the TOC present (average concentration: 8.6 mg/L) was estimated from the high PAC dosages data points.

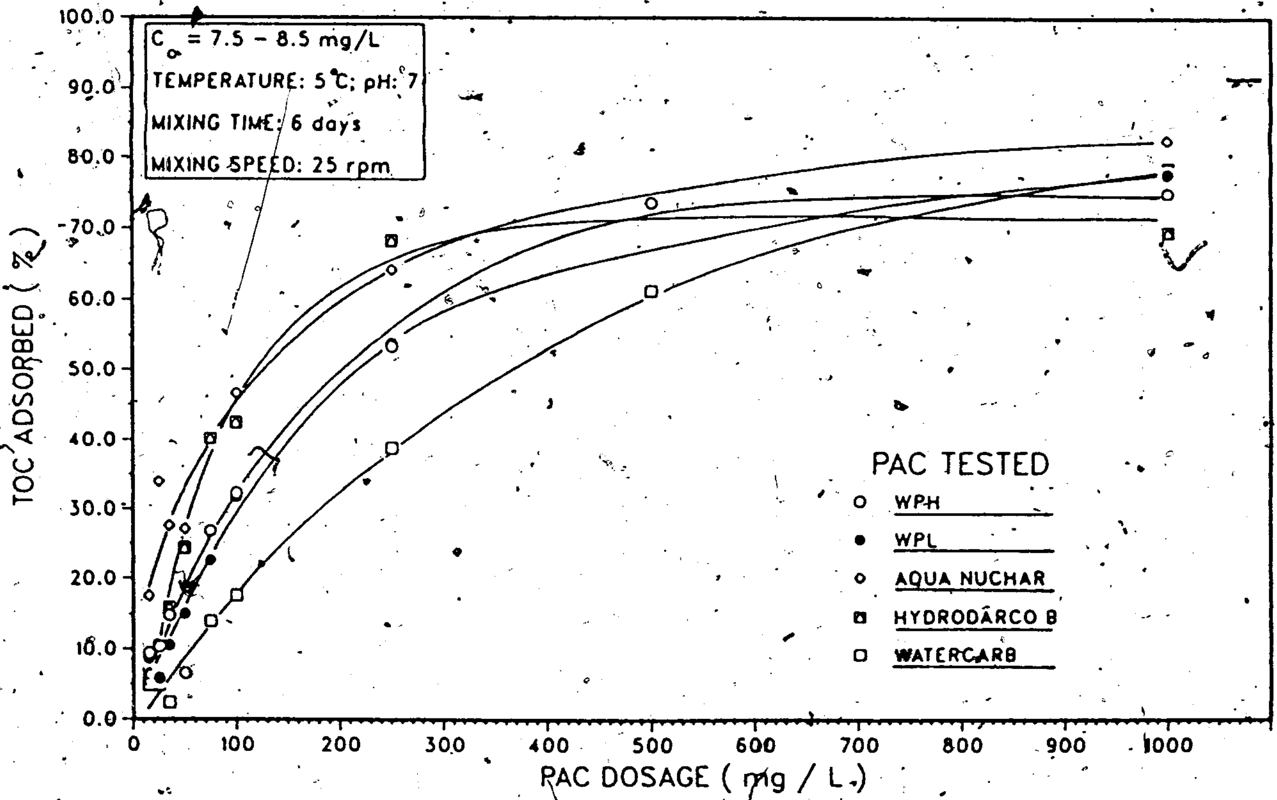

Figure 4.14 TOC adsorbed vs PAC dosage

5. DISCUSSION

5.1 Discussion of Results

5.1.1 Iodine Number

The iodine number test is carried out as a one point isotherm. The amount of iodine adsorbed per mass carbon is determin[illegible]tacting the iodine solution with only one dosage of activated carbo[illegible]tical isotherm slope (carbon loading per iodine solution concentration) is then assumed for each activated carbon tested, to estimate the capacity at a fixed residual concentration. Since the derivation of the iodine number is based on the assumption that the activated carbons tested are equally affected by the solution concentration, in the initial to residual concentration range, it must be used with care. Also, since the effect of concentration on adsorption capacity is not taken into account, information such as the adsorption behaviour of individual carbons for iodine or any other groups of compounds, cannot be inferred from the result of this test. The iodine number test gives only the carbon's capacity for iodine at a high initial concentration. /

However, the test can provide an estimate of the specific surface area for adsorption of iodine, if the carbon is completely saturated with iodine, that is, if a complete monolayer is formed, and if the carbon loading is constant and maximum over the concentration range present, and if it is assumed that a second layer is not formed (Langmuir model) (Kipling, 1967; Weber, 1972). With the knowledge of the molecular area of iodine and of the orientation of the molecule as it is adsorbed on the carbon surface, the active surface area can be computed. Therefore, the surface area available for iodine adsorption per gram carbon is directly related to the amount of iodine adsorbed per gram carbon, if the conditions above-mentioned are met.

The validity of the iodine number test thus depends on numerous assumptions which were not verified, to my knowledge, for activated carbons as they are produced now.

The execution of the test itself also brings about two weaknesses which could be modified, that is: the mixing time and the carbon wetting. The purpose of the latter is to homogenize the surface chemistry of the activated carbon. However, the effect of contacting the carbon with hydrochloric acid prior to adsorption can differ from one carbon to another. Mixing the carbon with the iodine solution for only 30 seconds may not constitute a sufficient contact time to form a complete monolayer of the adsorbate on the porous surface of the carbons.

The precision of the procedure is dependent mainly on the titrations performed to normalize the reagents and to measure the solution normality. Triplicate measurements of the iodine number for each carbon resulted in relative standard deviations of 0.22 to 2.4%.

The iodine number results will be compared to the organics adsorption tests performed in this study, to examine any possible correlation which could allow us to confirm or disprove the initial evaluation of the test.

5.1.2 Tannin Value

According to the tannin value test results (Figure. 4.3), the activated carbons designed for water treatment have a limited adsorption capacity for the high molecular weight compound tannic acid.

The structure of tannic acid (gallotannic acid: penta-m-digalloyl-glucose; M.W.: 1701.24) is similar to that of tannin, which is an amorphous substance found in parts of trees and shrubs (Kingzett's, 1966; Miall's, 1981). But it is difficult to determine if tannic acid possesses characteristics common to the group of polymeric organic acids known as the humic substances (humic and fulvic acid), which do not include tannins (Thurman, 1985). The exact structure of aquatic humic substances is unknown and probably continuously changing; their molecular weight can range from 500 to 5000. The commercial substitutes for humic and fulvic acid have been shown to be significantly different (based on C

NMR spectra) from the humic substances isolated from streams and soils (Malcolm and McCarthy, 1986). Therefore it is not possible to assess the validity of the use of tannic acid as a substitute compound for humic substances in adsorption tests, based on a knowledge of these organics.

Analysis of the results of the tannin value test shows that the adsorption of tannic acid follows the Freundlich isotherm model well except for the carbon PAC 20B. Losses in precision can be caused by differences in amount of carbon weighed and carbon contacted with the solution; inaccurate measurement of the volume of solution; presence of carbon on the paddles; errors in the absorbance measurement, and in calibration of the spectrophotometer.

5.1.3 Adsorption of Phenol

The modified phenol value test really only states the adsorption capacity of activated carbons for phenol, under the specific conditions of the test (pH, temperature, high initial concentration). Extending the results of the modified phenol value test to the adsorption of low lolecular weight compounds which cause taste and odour, as is often suggested in the commercial activated carbon literature, is premature. Furthermore, it is not possible to extend the affinity of carbons for phenol to phenolic compounds in general: solvent-solute interactions and solute-carbon interactions can differ. According to Al-Bahrani and Martin

(1976), the introduction of a CH_4, OCH_3, Cl, CH_3 or NO_2 group to the phenol molecule hinders the formation of the hydrogen bond between the hydroxyl group and water, thus resulting in better adsorption of the related phenolic compounds. The effect of the carbon's surface chemistry on the adsorption of phenol and p-nitrophenol was recognized by Snoeyink *et al.* (1969). They noticed significantly better adsorption of phenol on a coal base carbon than on a coconut shell carbon, although it had a smaller surface area. This affinity was not found for p-nitrophenol.

Good confidence in the estimated modified phenol value is justified by the narrow 95% prediction interval (Table 4.8). The test uses a high phenol concentration, therefore losses due to volatilization are relatively insignificant. The calibration of the spectrophotometer also yielded a regression line with a coefficient of 99.9%.

Correspondence between the grading of the PACs by the modified phenol value test and by the iodine number test is limited. For example, the iodine number did not suggest the superior adsorption capacity of Watercarb for phenol.

A comparison of the modified phenol value test with the phenol isotherm test at a lower initial concentration shows that a similar grading of the PACs is obtained (see Figures 4.4 and 4.5). However, due to more important variations in slope, the carbons are not as easily graded as with the modified phenol value test. On the other hand, differences in the adsorption behaviour of the carbons tested are more visible. The PAC Aqua Nuchar exhibited much lower carbon loadings at lower equilibrium concentrations. This is not advantageous since it means that high dosages of Aqua Nuchar are required to achieve significant reductions in phenol concentration. The low efficiency of this carbon was not detected with the standard phenol adsorption test.

Consequent to the lower phenol concentration used, losses by volatilization and in the procedure are more significant. The phenol concentration in the blanks varied by 8% (relative standard deviation). A list of the sources of errors would include: losses of phenol incurred during mixing and fill-up procedures; losses of carbon upon bottle fill-up; GC calibration; variations in the detector's response and in the integration of the peaks area counts due to variations in peak shape.

A further modification of the phenol test was the use of river water as the background for adsorption, with phenol at an initial concentration of approximately 7 mg/L. The natural alkalinity of the water was relied upon to act as a buffer. The pH of the phenol solution was 7.8, a pH in the range of values expected in the raw water at the point of PAC addition at the Rossdale Water Treatment Plant. The resulting phenol isotherms can be explained by the effect of pH and of competition from the organic and inorganic compounds in water.

In the pH range 6 to 8, phenol is mostly neutral (pKa: 9.9). Above a pH of 10, the adsorption of phenol is expected to decrease because it is mostly anionic and as such, repulsive forces between the negatively charged carbon and phenol, and between the phenol molecules themselves, will hinder adsorption. At a pH below 10, the capacity for adsorption is higher. However, it was observed by Snoeyink *et al.* (1969) that at a pH lower than 7.5, the adsorption decreased with pH. This occurrence was explained partly by an alteration of the nature of the carbon surface by the strong acid used to adjust the pH, and by the competition from the hydrogen ions for the carbonyl oxygen sites. In this study, the results of the adsorption tests show better phenol adsorption in river water than in deionized water for four out of six PACs (see Figures 4.7 to 4.12). The free hydrogen ions present at pH 6.5 in the phenol in deionized water experiment possibly competed for the adsorption sites (carbonyl functional groups) which are also sought by the phenol molecules. Therefore, better adsorption was obtained at pH 7.85 than at pH 6.0. The extent of this pH effect however, would depend on the surface chemistry of each activated carbon. A carbon which possesses a large fraction of carbonyl oxygens ie. which is more negatively charged, will adsorb less at a higher pH than a less anionic carbon.

Although it did not contain much TOC, the river water had a negative effect on the adsorption of phenol, particularly at low PAC dosages. This competition effect was compensated by higher dosages and maybe by the pH effect, for the PACs WPH, WPL, Watercarb, Aqua Nuchar and Darco S-51, but not for Hydrodarco B. The competition effect, important at low PAC dosages, was more significant for the carbons which showed greater adsorption capacity for tannic acid and TOC. These carbons can accomodate the larger molecular weight organics in the river water and thus, the passage of the small phenol molecules to the specific adsorption sites, can be limited or obstructed. From this observed trend, one could conclude that the application of a PAC which adsorbs tannic acid well (low tannin value) to the raw water would result in lower removals by adsorption of the low molecular weight compounds.

5.1.4. Adsorption of Mesitylene

The adsorption test for mesitylene did not result in a clear grading of the PACs, such as the one obtained from the phenol isotherms. However, the Calgon PACs distinguished themselves from the four other carbons. Their large superiority was brought about mainly by their flat slopes which indicate more efficient carbons, ie., carbons which can maintain a relatively constant loading as the equilibrium concentration in solution is decreased.

Lower regression coefficient values (R^2: 0.71 to 0.92) indicate that the regression using the Freundlich model does not explain all the variance in the results. The relative standard deviation of the concentration in the blanks was 12%. The error can be due to the relative volatility and lower solubility of mesitylene. Also, much lower PAC dosages were tested due to the expected superior adsorbability of mesitylene. Consequently, more error can be justified in the carbon weighing part of the procedure. This was tentatively compensated by using large bottles which would permit the use of a more manageable mass of carbon. Lower confidence is given to the GC calibration due to the instability of the prepared standards. On the other hand, the use of a capillary column yielded sharp peaks, easily integrated. Some contamination of the column was present as unexpected peaks appeared when standards were injected. These peaks were relatively inconsistant, appeared in all organic-free water samples from various sources, and were not detected in the distilled methanol. Analysis on a purge and trap GC-FID did not reveal the presence of any organics. It was therefore assumed that they were being slowly eluted from the column when water was the solvent. These peaks interferred at times with the mesitylene peaks; injections were then repeated.

Limitations to the isotherm procedure must also be acknowledged. In order to minimize losses, all unessential transfer steps were eliminated. After adsorption and centrifugation, the supernatant was not transferred into a storage bottle; rather, it was immediately analyzed directly from the centrifuge tubes. This does not permit any flexibility for the quantitative analysis and requires that only one PAC be tested at a time.

Mesitylene is more easily adsorbed than phenol in deionized water, as shown by a comparison of their K values. This is partly due to mesitylene's lower solubility, thus its greater affinity for carbon than for water, but also due to phenol's hydroxyl group which can form a strong hydrogen bond with water. However, the capacity for mesitylene rapidly decreases with decreasing equilibrium concentration, except for WPH and WPL.

A comparison of the two tests must take into account the differences in test conditions. Mesitylene was advantaged by the lower temperature of the experiment. The pH (8.0) may not have affected the adsorption of mesitylene, since it is not ionic, however, the adsorption of phenol at a pH 8.0 may have been more complete.

The most obvious observation from this comparison is the low adsorption capacity of Watercarb for mesitylene, compared to phenol. It seems that Watercarb, has a surface chemistry which is favourable to the specific adsorption of phenol by an electron acceptor-donor complex, but not for less polar aromatics, as indicated by mesitylene. If one was to base the selection of PACs on the adsorption of phenol, Watercarb would have been the first choice. However, a criteria based on mesitylene adsorption shows Watercarb to be equivalent to the Norit PACs. It is therefore possible to see the effect of evaluating the performance of PACs on the adsorption of only one compound. Selection of a PAC with a particular affinity for that compound and an average adsorption performance for other compounds is possible. However, a comparison of the behaviour of the other carbons show a similar grading as obtained with the phenol tests.

It is also interesting to note that the adsorption of mesitylene at high loadings corresponds to the grading obtained with the iodine number test.

5.1.5 Adsorption of TOC

The major fraction of TOC consists of humic substances (mainly fulvic acid), the composition of which is highly variable (Schnitzer and Khan, 1972; Thurman, 1985). The TOC adsorption test was meant to measure the extent to which PACs can adsorb the humic substances.

Unfiltered, 3 months old river water was used in this set of experiments. Therefore, flocculation of particulate matter and coagulated dissolved organics, as well as some biodegradation may have occured during the 6 days mixing period, which will have changed the composition of the water. Measurement of the TOC content, with a TOC analyzer, is based on the assumption that all organic carbon has been oxidized when the inorganic carbon is measured. Human error is also involved with manual injections and instrument calibration. The TOC isotherm results fitted poorly the Freundlich model used to analyze the other experimental results; it was thus difficult to interpret and compare them.

Nonwithstanding the uncertainties with the TOC isotherms, it can still be considered, for discussion purposes, that the TOC was representative of the humic substances, possibly more so than tannic acid. Also, the tannic acid isotherm parameter K and the tannin value both follow a similar grading as obtained for the TOC adsorption test. The grading is the same when TOC is compared with the higher loadings of tannic acid. The tannic acid test can therefore be used to determine the adsorption capacity for TOC (humic substances) and estimate which PAC will be negatively affected by relatively high concentrations of dissolved organics and other compounds.

5.1.6 Conclusions

Comparison of PACs

- Calgon's WPH and WPL have equivalent adsorption capacities for all compounds tested.
- Aqua Nuchar (Westvaco) displayed low adsorption efficiency for phenol, mesitylene and TOC.
- Watercarb (Husky) has an affinity for phenol.
- Darco S-51 and Hydrodarco B (Norit) have low adsorption capacities for phenol, mesitylene and iodine but superior capacity for TOC and tannic acid.

Comparison of Adsorption Tests

- The iodine number test can give an indication of the available surface area for the adsorption of iodine. It does not take into account the effect of concentration on capacity nor specific adsorption mechanisms, therefore it cannot replace a complete adsorption test for specific low molecular weight organic compounds. The grading of the carbons obtained with this test was repeated only with the mesitylene adsorption test at high loadings. However it did generally confirm the trend observed with the phenol and mesitylene tests, that WPH, WPL, Aqua Nuchar and Watercarb have better adsorption capacities for low molecular weight compounds than Darco S-51 and Hydrodarco B.
- A phenol adsorption test cannot be used as the sole

basis for the selection of a PAC because of the possibility of a specific interaction of phenol with the carbon surface. The modified phenol value test can be used to show the affinity of carbons for phenol only. A test with a lower initial concentration does provide more information on the adsorption behaviour of carbons for phenol, however, the degree of inaccuracy in the test increases.

- Comparison of the adsorption of mesitylene with the adsorption of phenol revealed the differences in adsorption behaviour of PACs with respect to polarity. Although the test procedure could be made more flexible in its execution, it should be integrated into a temporary PAC selection protocol in order to supplement the phenol adsorption test.
- On the basis of the limited TOC adsorption results, the tannin value test gives an indication of the adsorption capacity for TOC and humic substances. According to the phenol in river water adsorption isotherms, it can be used to assess the extent of the impact of the presence of TOC on the adsorption of lower molecular weight organics.
- The tests performed did not allow the drawing of conclusions with respect to the effect of particle size distribution on adsorption capacity. The particle size and density of an activated carbon will mainly affect its suspendability and filterability.

5.2 Testing Protocol

The objective of a testing and selection protocol for commercial PACs is to determine which PACs possess the most appropriate characteristics for the adsorption of the majority of organics of concern in the raw water and to select the most cost-effective PAC.

In order to establish this testing protocol, it is necessary to consider the following elements:

- the organic and inorganic composition of the raw water, and the variability in its content.
- the knowledge of the organic compounds which should be adsorbed: the taste and odour causing compounds and possibly the precursors to odorous compounds.
- the conditions under which PAC must adsorb those organics, particularly: the operational parameters and the presence of competing species.
- the selection of surrogate testing compounds which can give an indication of the adsorption capacity of PAC for the organics which may cause taste and odour.
- the degree of information on PAC performance expected from the testing protocol.
- the analytical procedures and time period available to evaluate the PAC samples.
- the validity and usefulness of the existing standard tests and parameters devised to characterize the PACs.
- the extension of the testing protocol to the

establishment of purchasing and quality control criteria.

The testing protocol will thus have to take into account the current state of knowledge and characterization of the water to be treated, and an awareness of the multiple interactions of the adsorption process in a complex water matrix.

In Edmonton, and particularly at the Rossdale Water Treatment Plant, two distinct types of spring runoff have been observed to result in decreased aesthetic quality of the drinking water: the street runoff, at the first major snow melt, brings a high load of alkanes and some aromatics from the storm sewer disharges; the upstream runoff, which can occur almost concurrently to the street runoff and also later in the spring when the upstream reservoirs are opened, discharges water laden with humic substances and some simpler carboxylic acids. Odorous microbiotic byproducts, such as geosmin and MIB, can also be present in this type of runoff, although their presence has not been confirmed. During each episode, PAC is added to the raw water in an attempt to remove some of the taste and odour causing compounds or the precursors to the odorous compounds which may be formed later in the process. The organic content of the raw water and the treated water at the peak of the 1986 spring runoff, both urban and upstream, has been partially analyzed and compounds identified by GC/MS. Types of compounds which may be causing the foul tastes and odours have been suggested from a classification of customer complaints. They are: hydrocarbons, ch[illegible]ated phenols, chloramines and algae or bacterial metabolites (Walker *et al.*, 1986). Classification of the odours on the basis of their probable origin, biological (humic substances, metabolites), anthropogenic (hydrocarbons) and from disinfection with oxidants, has been validated in 1986. However, confirmation of the exact causes of taste and odour occurrences has not been achieved with a sufficient degree of certainty. Variations in the character and intensity of the odour of both the raw and drinking water over the spring runoff period and from year to year, indicate that the taste and odour occurrences are caused by a varied group of compounds and can be the result of synergistic interactions. Therefore, considering the lack of knowledge of the origin of the taste and odour in the water, it is not possible to evaluate PACs on the basis of their capacity to adsorb the specific taste and odour causing compounds.

The taste and odour causing compounds are thought to be mainly present at trace levels in a complex mixture of organics, the major part of which consists of macromolecules such as humic substances, proteins, polysaccharides and hydrophilic acids (Thurman, 1985). Therefore, their adsorption is hindered by competing molecules which, although they do not necessarily adsorb to the same extent as the low molecular weight compounds, can block the access to the adsorption sites. PAC is added concurrently with alum and chlorine dioxide, thus reducing further its adsorption efficiency. The extent of the competition due to the background organics will vary as the quality of the raw water changes, and will affect each compound differently. Therefore the adsorption performance of a PAC for a specific compound in the river water matrix may vary with the raw water content. Thus, comparing the adsorption capacity of PACs using the river water at the time of PAC selection may result in a performance which differs from the adsorption capacity at spring time.

The mixing time and speed during the coagulation step, as well as the total contact time of the PAC with the organics may also influence the extent of adsorption of particular compounds. In a bench-scale testing procedure, based on bottle-point adsorption isotherms or jar-test procedures, a state of equilibrium is sought by increasing the contact time. However at the plant, under the actual conditions, adsorption of some compounds with a slower rate of adsorption may be limited, even though this is not measured in an isotherm test. Therefore, a bench-scale testing protocol which simulates closely the plant conditions may not result in the selection of the ideal PAC because of the variability of the water content with time and the possible effect of the process parameters such as mixing speed, contact time and presence of added chemicals.

Since specific taste and odour causing compounds cannot be used in the testing protocol, surrogate compounds must be chosen which can provide an indication of the potential for adsorption of the tested PACs. The limitations on any adsorption tests stemming from the variability of the river water and the influence of interactions within the water matrix on the adsorption process, must be taken into account as the surrogate compounds are chosen and their adsorption results analyzed. Selection of the testing compounds can be based on the suggested sources of taste and odour occurrences and on the water analyses of previous years, but mainly, results of adsorption tests must provide a general guidance towards the overall potential capacity of a PAC. As generalizations cannot be readily made with respect to adsorption, only a few characteristics can be derived, mainly: indications of its pore size distribution, its surface area and its surface chemistry. In this study, the adsorption of iodine, phenol and mesitylene, tannic acid and TOC, was analyzed. The extremes of molecular sizes were tested, thus revealing the range of molecular sizes the PACs can accommodate for adsorption. An indication of the surface area for the non-specific adsorption of a low molecular weight compound was provided by the iodine test. A comparison of the phenol and mesitylene adsorption isotherms allowed a differentiation of the PACs based on their interactions with ionic species. However, an extension of the results to predict the adsorption behaviour for other compounds was not made, other than to say that carbons can be categorized on the basis of their capacity to adsorb low molecular weight or high molecular weight compounds and that trends were detected which may be thought to apply to other compounds. An example of this last statement would be the PAC Aqua Nuchar which repeatedly indicated low efficiency as the equilibrium concentration decreased. Therefore, unless the testing protocol is based on the specific adsorption of the compounds to be removed, it can only give information on the physical characteristics of the activated carbons.

It is clear that more tests can be devised to examine the adsorption of more compounds, thus confirming or improving the evaluation of a PAC. The formulation of additional tests is however governed by analytical procedures required to generate the results. For example, in this study, the mesitylene adsorption isotherm experiments were run to compare the PACs and to verify the results obtained by the phenol and iodine test. The test was devised weighing simplicity of procedure and quickness of analysis against quality and validity of the results. It would seem more appropriate to test the PACs for the adsorption of mesitylene at the concentration level at which it is found in the water, since extrapolation of isotherm data is not a recommended procedure. However, since the exact adsorption behaviour will not be reproduced in a bottle-point experiment, and concentration procedures are time-consuming and introduce additional sources of error, a higher concentration level was preferable. Also, measures had to be taken to limit the losses by volatilization of mesitylene. A more volatile compound would have required special apparatus where the solution is never contacted with the atmosphere. Such apparatus is not available in small laboratories. The chosen compound must also be relatively soluble in water at the concentrations tested. The batch solution of mesitylene, which has a solubility of approximately 20 mg/L in water, had to be prepared from a stock solution in methanol. The resulting methanol content of the solution was 1% by volume, a concentration which may have hindered the adsorption of mesitylene. Although the test procedure for the adsorption of mesitylene resulted in satisfactory isotherms which confirmed the general trend obtained by the phenol and iodine tests, it can still be improved. More compounds should be considered which can either replace mesitylene or supplement the adsorption test.

The tests included in the AWWA Standard for PAC and the tests performed by carbon manufacturers to characterize their products, must not be dismissed as useless because they do not test for specific compounds found in the water to be treated. Until the express purpose of PAC addition is defined, standard tests will be used. Their usefulness resides in their simple analytical procedures which is important when a large number of samples must be tested in a short testing time. However, inherent to their simplicity, are assumptions which must be weighed in the analysis of the results. For example, the adsorption of iodine is based on a constant isotherm slope for all carbons tested. The extent to which this assumed slope differs from the actual slope governs the error in the test. Also, the tests are performed under specific conditions which do not correspond to the conditions at a water treatment plant: temperature, pH, presence of competing species, degree of mixing and contact time can differ significantly. Nonetheless, performing the standard tests to evaluate PACs will reveal major trends such as the capacity of a group of carbons for the adsorption of humic substances or more polar low molecular weight compounds. In other words, standard test criteria allow the purchaser to distinguish categories of carbons, to screen out PACs which may not have the capabilities required, and retain a shorter list of PACs which can be reduced further on the basis of cost. Moreover, as the standard tests are routinely performed by the manufacturer, they are easily included in purchase specifications of bidding documents and in purchase contracts as criteria for quality control.

In summary, with the limited knowledge of the raw water composition and of the compounds which cause the taste and odour in the treated water, a testing protocol which includes the adsorption of specific problem causing compounds cannot be devised. Furthermore, the adsorption tests using surrogate compounds can only provide indications of the general adsorption capacity of carbons rather than predict the actual adsorption behaviour in the river water matrix. If the expectations from the testing protocol are thus revised, the usefulness of the standard tests and other simple adsorption tests is more easily acknowledged. Therefore, at the present time, a testing protocol which still makes use of the standard tests devised for this purpose is considered appropriate because no sufficiently determinative replacement can be devised with the information available.

6. GENERAL PROCEDURE FOR PAC SELECTION

Until PACs can be tested for the specific compounds which are known to be present in the raw water and causing taste and odour in the drinking water, surrogate compounds must be used in the testing protocol. The AWWA Standard for PAC has recommended the iodine number test and the modified phenol value test to assess the quality of PACs for water treatment, particularly taste and odour control. Although it is known that these tests do not provide a complete evaluation of PACs, and their limitations have been described, their usefulness has also been shown. From the adsorption tests performed in this study, the addition of tannic acid and mesitylene adsorption tests to the AWWA testing protocol can provide supplementary information on the adsorption behaviour of PACs. In fact, more surrogate compounds could be chosen to further complete the evaluation of a PAC. However, it must not be forgotten that an absolute assessment of the performance of a PAC cannot be obtained from bench-scale adsorption tests and that there is limited time to evaluate the samples provided in tenders.

The criteria chosen to screen PAC samples, or to be provided as minimum requirements in the bidding documents, should be based on the type of organics expected to cause the taste and odour problem. The minimum values suggested in the AWWA Standard are based on the general assumption that a PAC which can adsorb iodine and phenol well is preferable, since it is generally thought that taste and odour causing compounds are low molecular weight compounds present at trace level in the water. On this basis, the adsorption of tannic acid is not as important and should not be used as a screening criteria. A PAC which has a good tannin value does not usually suggest good capacity for lower molecular weight compounds. Therefore, the minimum values suggested by AWWA are recommended for screening.

In the course of the tenders evaluation, the carbon samples which meet the minimum requirements should be tested for their iodine number and for their capacity to adsorb phenol, mesitylene and tannic acid. The analysis of the results should be based on the complete isotherm obtained rather than on a single point estimate such as the suggested modified phenol val or tannin value. In addition to being a better representation of the adsorption capacity, it permits a verification of the quality of the results and of the range of dosages used. To select a PAC with a higher potential for adsorption of low molecular weight compounds, the iodine number should exceed 600 mg/g. The carbon which shows good adsorption capacity for both phenol and mesitylene, and which does not adsorb tannic acid well should be considered. In general, PACs which display steep isotherm slopes, thus indicating low adsorption efficiency with respect to dosage, should be avoided. If more than one PAC is adequate, the final selection should be made on the basis of cost.

In the advent that a PAC which has a higher adsorption capacity for TOC (or UV absorbance) is considered more appropriate, for example, if the upstream runoff, bringing high loads of colour and humic substances which could be partially handled by activated carbon adsorption, is considered more troublesome, then the tannic acid test should be given more weight in the analysis. In fact, if PAC is added for the sole purpose of adsorbing TOC, then the PAC with the highest capacity for tannic acid should be selected, without consideration of the other test results. Selection of a PAC with good adsorption capacity for tannic acid would virtually exclude PACs with high capacities for phenol, iodine and mesitylene, according to the trends observed in this study.

Quality control of the PAC purchased should be aimed at verifying the consistency of batches and therefore be based on the particle size distribution, the density and iodine number only. However, monitoring the performance of the PAC during treatment based on the reduction in odour is important to ensure that an appropriate PAC was chosen and to help in future adjustments to the selection protocol.

7. SUMMARY AND CONCLUSIONS

A review of the literature on the adsorption of organics in water on activated carbon has shown that the adsorption rate and capacity depends on the internal surface area, the pore size distribution, the particle size and the presence of oxygen-containing functional groups on the surface of the carbon. The properties and characteristics of the individual compounds such as their solubility, polarity, molecular size and degree of ionization, although significant in single-solute adsorption systems, are only of relative importance when dealing with a complex matrix such as river water. The competition effect from the large number of compounds present in the water as well as from the chemicals added for water treatment such as coagulants and oxidants, will affect the adsorption behaviour of selected compounds. Also, the water pH will influence the interaction between polar activated carbons and ionic species.

Powdered activated carbon has been applied at a large number of water treatment plants in an attempt to control taste and odour occurrences, due to biological and man-made causes, as well as to reduce colour and the THM formation potential. The variations in performance from one plant to another depend on the type of organics to be adsorbed, on the water matrix and on the type of PAC used.

The standard tests which currently serve to evaluate PACs for water treatment have been devised from the tests on decolourizing carbons in the sugar industry. The iodine number test, the modified phenol value test and the threshold odour test are the most common. However, their appropriateness for the assessment of PACs for taste and odour control has long been a subject of discussion.

To determine an appropriate selection criteria, eleven PAC samples were tested for their particle size distribution, their iodine number and their adsorption capacity for tannic acid. Of those, six samples were selected and tested further for their adsorption capacity for phenol, mesitylene and TOC, in an attempt to verify if standard tests can replace full-fledged adsorption isotherm tests with chosen surrogate compounds under more valid conditions. The results of the testing can be summarized as follows:

- The PACs tested can be broadly classified into two groups: the PACs which can adsorb high molecular weight compounds, as measured by TOC and tannic acid; and the PACs which adsorb better the lower molecular weight compounds such as phenol, mesitylene and iodine.
- Based on the phenol adsorption test, the grading of the PACs did not change as the initial concentration in the adsorption test was reduced from 200 mg/L to 10 mg/L phenol.
- The grading of the PACs did not change as river water

was used as the background matrix rather than deionized water, in the phenol adsorption tests.

- The background organics reduced the adsorption capacity for phenol. This negative effect was compensated by higher PAC dosages.
- The PACs which have a higher adsorption capacity for tannic acid and TOC were more negatively affected by the presence of river water, when measuring phenol adsorption.
- A comparison of the mesitylene adsorption isotherms and the phenol adsorption isotherms showed that the PAC Watercarb may have a particular affinity for phenol, due to its surface chemistry.
- The mesitylene adsorption test results demonstrated the significant superiority of the PACs WPH and WPL.
- The standard tannin value test and the TOC adsorption test yielded similar gradings of PAC performance.

From an analysis of the results, the following conclusions were drawn:

- If a PAC with a large fraction of micropores is required, the iodine number test should be used to screen out the PACs which do not have a large internal surface area.
- Since the phenol adsorption tests at lower initial concentration yielded similar gradings of PACs as obtained with the modified phenol value test, the latter should

be used to evaluate PACs with respect to their adsorption capacity for phenol.

- A PAC chosen to adsorb preferentially low molecular weight compounds should not display a high capacity for tannic acid or TOC.
- The evaluation of PACs cannot be based on the adsorption capacity for one compound only. The phenol adsorption test alone or in combination with the iodine number test is insufficient to select an appropriate PAC. A series of adsorption tests covering a wider range of compounds can better display the adsorption trends and characterize the PACs. However, the selection of these compounds should not only be based on their validity as surrogate compounds, but also on the analytical procedures available to quantify them.
- The mesitylene adsorption test can supplement the standard tests by providing additional information on the adsorption of a non-polar aromatic hydrocarbon.
- A testing protocol which makes use of the AWWA standard tests, supplemented by the mesitylene adsorption test is recommended, if the cause of the taste and odour episodes has not been determined, as is the case at the Edmonton Water Treatment Plants.
- The evaluation of the PACs should be done on the basis of the complete adsorption isotherms rather than one point estimates such as the tannin value or the modified phenol value.

The testing protocol, as performed in this study can be further improved. In the modified phenol value test, the addition of a buffer solution which brings the pH more closely to the required test pH would eliminate the need for a large volume of concentrated acid. In the mesitylene adsorption test, the test solution could be prepared and contained in such a manner as to minimize the contact with the atmosphere and consequent losses by volatilization. A teflon lid, floating on the surface of the solution as it is mixed and pumped out to fill bottles, could be added to an appropriately cut carboy.

Finally, the selection of a PAC would be successfully completed with a monitoring program to evaluate its performance during treatment of low quality raw water, with respect to the reduction in odour, volatile organics, extractable hydrocarbons, UV absorbance or TOC. Confirmation that an appropriate PAC was chosen would then be achieved.

8. RECOMMENDATIONS FOR FURTHER RESEARCH

- The characterization and quantification of the organic content of the raw water and the treated water must be completed. The major causes of the taste and odour occurrences must be determined to a greater extent in order to define more precisely the compounds which the PAC is applied to remove.
- When the organics causing the taste and odour in the raw water have been identified, a specific adsorption test using this or these compounds should be devised, using the raw water as the background matrix.
- The effect of the presence of alum and chlorine dioxide at the PAC contact point should be investigated. Alternative sequences of treatment processes should be considered if it is found that PAC can improve the taste and odour control performance significantly.
- The effect of solute concentration on the adsorption capacity, at the PAC dosages used, could be further assessed, to determine if differences between PACs observed at mg/L concentration levels exist also at the µg/L and ng/L levels.
- The appropriate PAC dosages should be determined by monitoring the threshold odour number during taste and odour occurrences. The maximal practical dosage which can be applied without serious reduction in filter performance, should be evaluated for the PAC currently used.

- Improvements to the contacting method could also be investigated and the possibility of increasing the contact time by adding the PAC ahead of the rapid mixing. At the Rossdale Water Treatment Plant, since PAC is added at different points for the plants #1, 2 and 3, a comparison of their performances could be done.

Since two types of spring runoff are distinguished in Edmonton, it may be appropriate to try two different PACs with characteristics more favourable to the adsorption of the type of organics present at each episode. This would only be justified after a complete characterization of the water has confirmed the origin of the taste and odour problems. It may be desirable to add PAC to assist the coagulation-flocculation process in the removal of the humic substances present in the upstream runoff.

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APPENDIX 1. List of PAC Manufacturers and Suppliers

Table A.1 List of PAC manufacturers and suppliers

PAC	MANUFACTURER & ADDRESS	SUPPLIER & ADDRESS
AquaPac AquaNuchar	Westvaco Chemical Division Carbon Department Covington, Virginia,24426 (703) 962-1121	Harrisons & Crosfield Ltd P.O.Box 5586, P.Station L Edmonton, Alberta, T6C 4E9 (403) 440-2233
WPH WPL	Calgon Carbon Corporation P.O.Box 717 Pittsburg, PA,15230-0717 (412) 787-6700	same as Manufacturer
Watercarb Watercarb Plus	Husky Charcoal Sales, Inc. Route 5, Box275 Dunnellon, Florida,32630 (904) 489-3336 1-800-874-3302	same as Manufacturer
Norit W-20	Norit Activated Carbon P.O.Box 105 3800 AC Amersfoort The Netherlands 33-30454	VanWaters & Rogers Ltd. 64 Arrow Road Weston, Ontario, M9M 2L9 (416) 741-9190

Table A.1 List of PAC manufacturers and suppliers, continued

PAC	MANUFACTURER & ADDRESS	SUPPLIER & ADDRESS
Darco S-51 Hydrodarco	American Norit Company Inc. 6301 Glidden Way Jacksonville, Florida, 32208 (904) 765-3584	VanWaters & Rogers Ltd. 64 Arrow Road Weston, Ontario, M9M 2L9 (416) 741-9190
WTC	Transpacific Carbon Co.	Mackenzie & Feimann Ltd. 12835-146th Street Edmonton, Alberta, T5L 2H6 (403) 451-9222
PAC 20B PAC 20C	Atochem Inc.Ceca Division 4150 S.100E.Ave., suite 300 Tulsa, Oklahoma, 74146 (918) 660-0606 1-800-331-5610	Mackenzie & Feimann Ltd. 12835-146th Street Edmonton, Alberta, T5L 2H6 (403) 451-9222

APPENDIX 2. Typical Characteristics of PACs

Table A.2.1 Typical physical characteristics of PACs, as given by the manufacturers

PAC	Source material	Type of activ. process	Apparent Density (kg/m^3)	Particle size distrib. (% passing #) 100-200-325	Ash content (%)	Moisture content (%)
Aqua Nuchar			641 max.	99 - 97 -90		5 max.
Aqua Pac			737 max.	99 - 97 -90		5 max.
WPH	coal	thermal	641 max.	99 - 97 -90	9.3	5 max.
WPL	coal	thermal	641 max.	99 - 95 -90		5 max.
Watercarb	wood		450-510	99 - 95 -90	1.5 max.	5 max.
Watercarb Plus	wood		450-510	99 - 95 -90	1.5 max.	5 max.
Norit W-20	peat		600	97 - 90 -78	6 max.	2
Darco S-51						
Hydrodarco B						
WTC	wood	thermal	400	-90	7	
Pac 20B	coal		490-580	95 - 85 -70		2 max.
PAC 200	coal					2 max.

Table A.2.2 Typical adsorption characteristics of PACs, as given by the manufacturers

PAC	Iodine number (mg/g)	Phenol value (mg/L)	Modified phenol v. (g/L)	Methylene blue ads. (%)	Molasses number	Decolorizing index
Aqua Nuchar	800 min.		2.2 max.			9 min.
Aqua Pac	600 min.					
WPH	800 min.		2.2 max.		266	
WPL	500 min.		3.5 max.			
Watercarb	550 min.		1.82 - 2.28			
Watercarb Plus	650 min.		1.59 - 2.05			
Norit W-20	700	18		5		
Darco S-51						
Hydrodarco B						
WTC	500				100	
PAC 20B	800 min.		2.4		190 min.	
PAC 200					260 min.	

APPENDIX 3. Calibration Curves

- Tannic acid calibration curve (UV spectrophotometer)
- Phenol calibration curve (UV spectrophotometer)
- Mesitylene calibration curve (GC-FID)
- Phenol calibration curve(GC-FID)

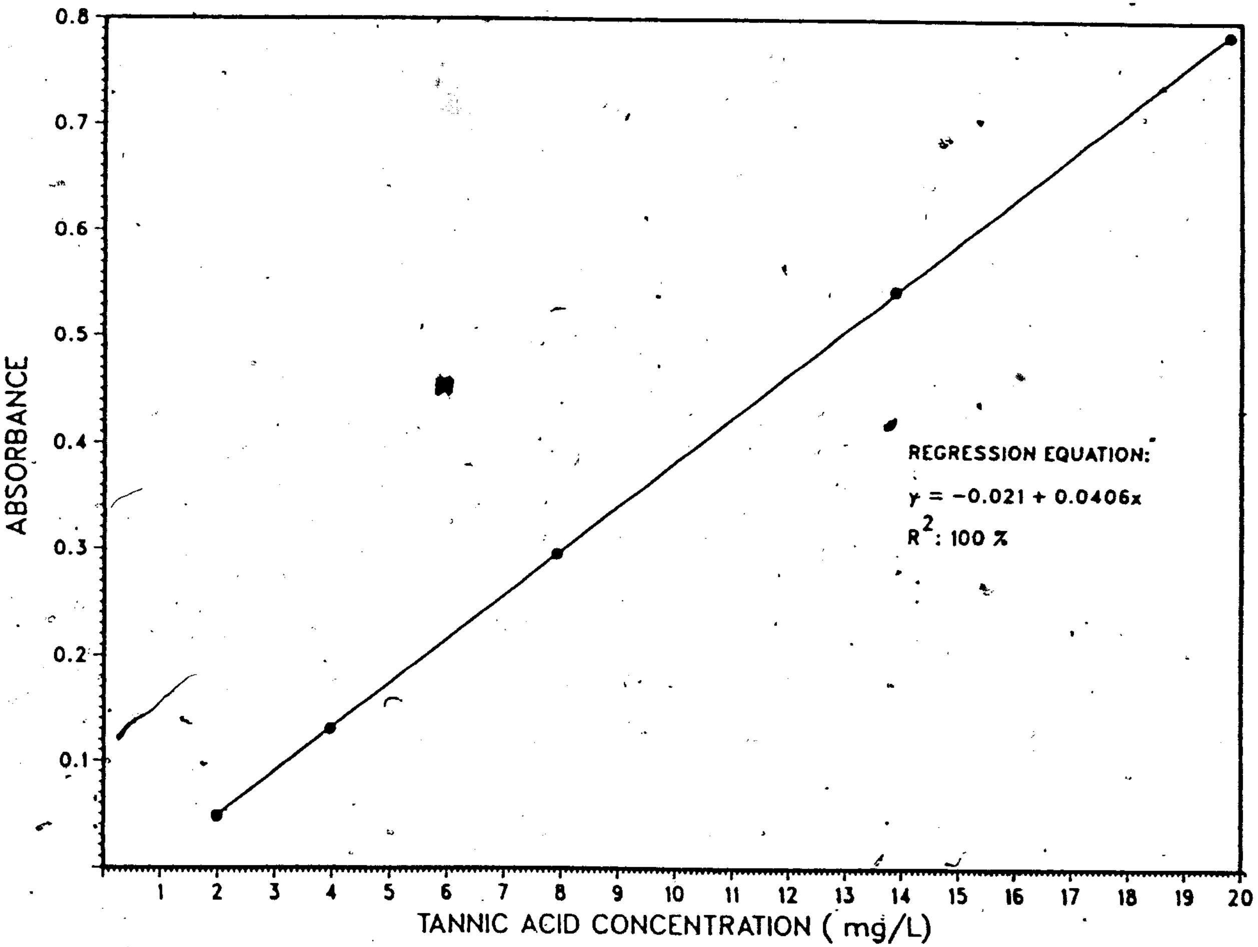

Figure A.3.1 Tannic acid calibration curve

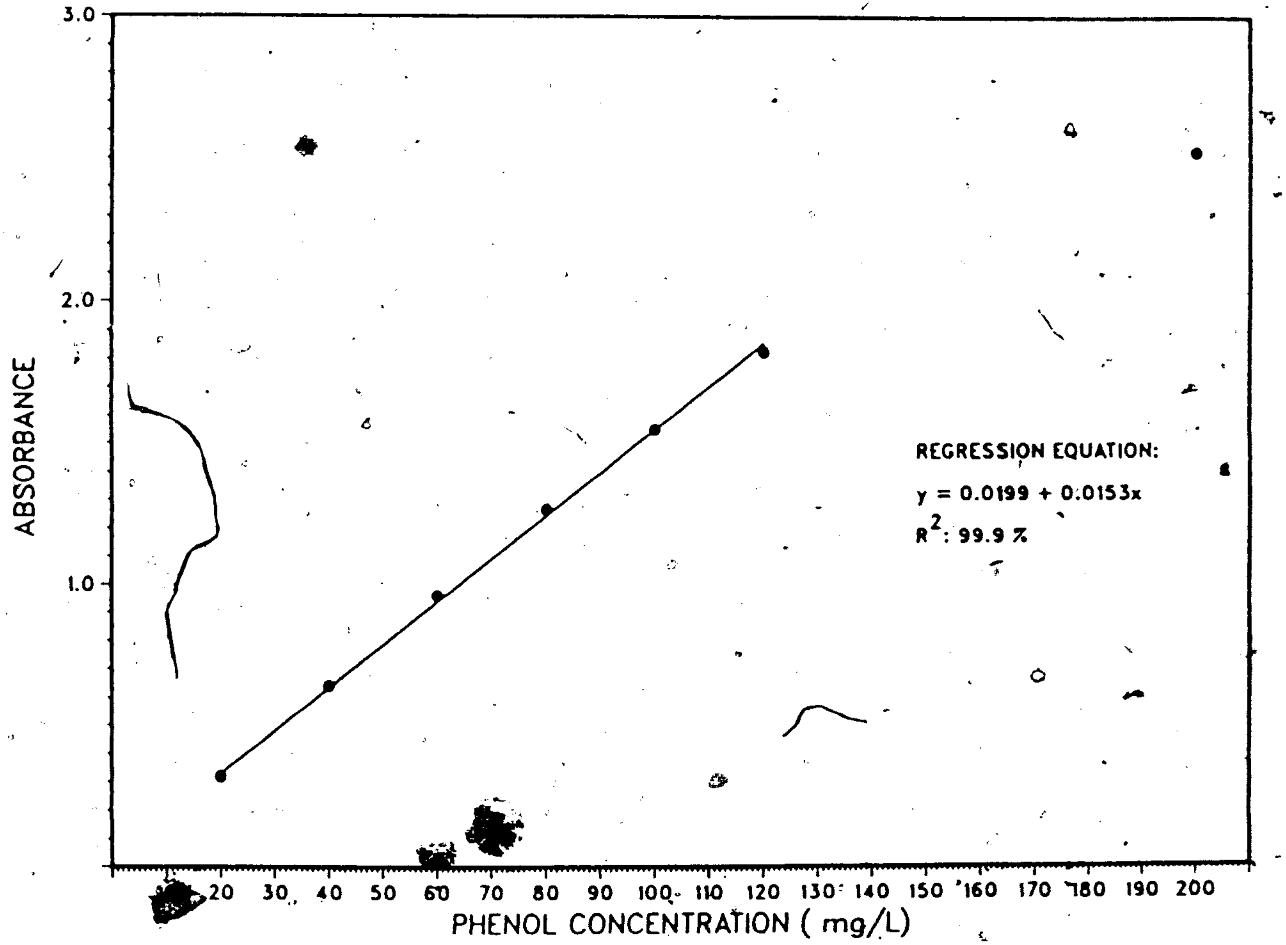

Figure A.3.2 Phenol calibration curve - UV

Table A.3.1 Mesitylene calibration curve data

Standards concentration (mg/L)	Area count	Average area count	Standard deviation (%)
0.22	4 307 4 355	4 331	0.78
1.1	17 183 14 618 14 562	15 454	9.7
5.5	77 751 78 278 83 337	79 789	3.9
7.7	117 340 116 920	117 130	0.25
11.0	152 950 151 340	152 145	0.75

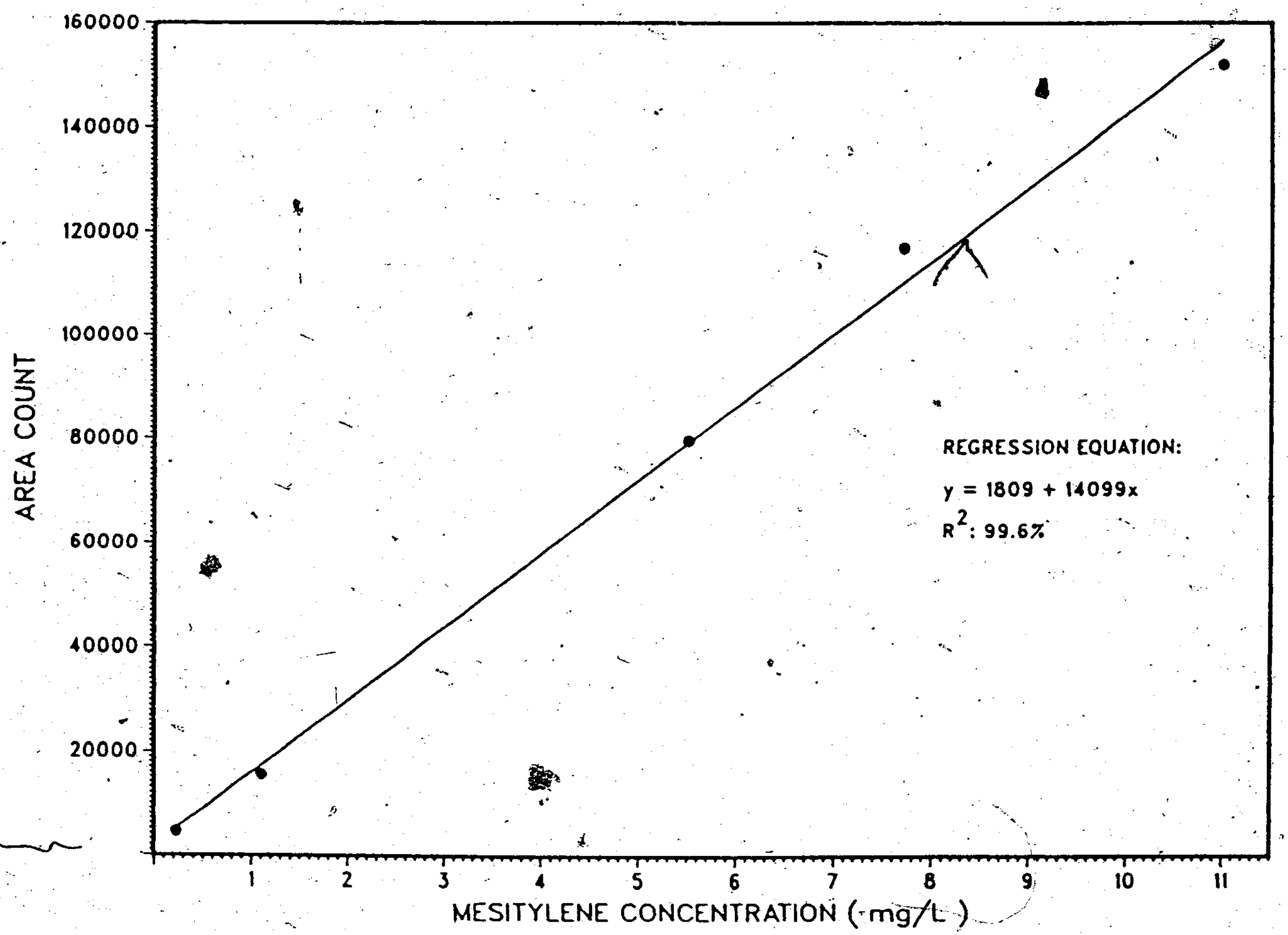

Figure A.3.3 Mesitylene calibration curve

Table A.3.2 Phenol calibration curve data (March 08, 1987)

Standards concentration (mg/L)	Area count	Average area count	Standard deviation (%)
0.499	25 635 24 541	25 088	3.1
0.998	43 880 37 282 38 738	39 965	8.7
1.99	68 284 57 715 47 469	57 756	18.0
2.99	76 300 84 792 80 374	80 489	5.3
4.99	148 650 137 260 128 240 131 [illegible] 1[illegible]	132 158	9.3
9.98	2[illegible] 231 37[illegible] 266 770	264 527	12.1

Table A.3.3 Phenol calibration curve data (March 09, 1987)

Standards concentration (mg/L)	Area count	Average area count	Standard deviation (%)
1.99	55 177 57 217 50 255	54 216	6.6
4.99	118 220 117 610 117 220	117 683	0.43
9.98	221 940 201 490 219 950	214 460	5.3

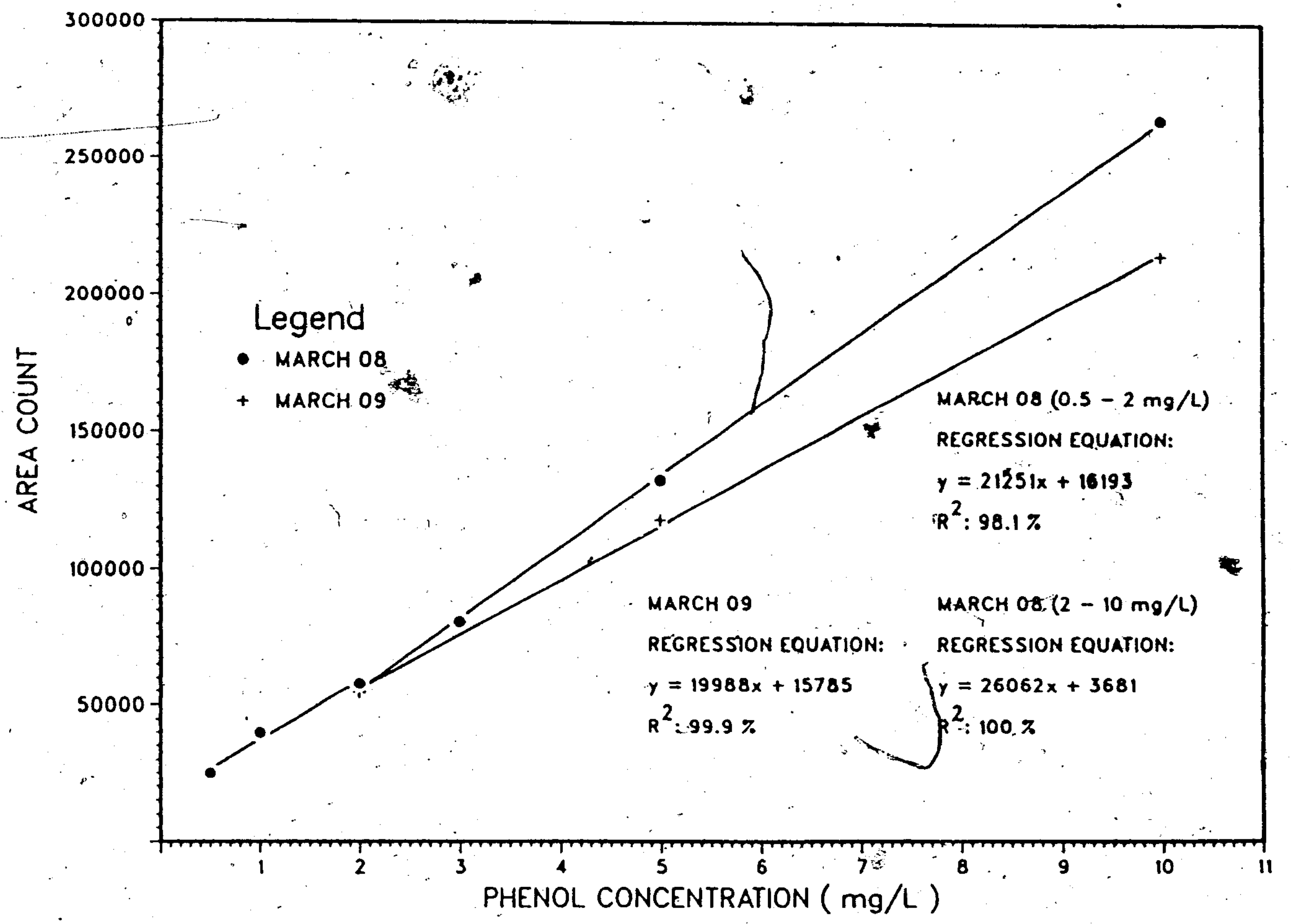

Figure A.3.4 Phenol calibration curve - GC-FID

APPENDIX 4. Verification of the Mesitylene Test

A.4 VERIFICATION OF THE MESITYLENE ADSORPTION TEST PROCEDURE

The test for the adsorption of 1,3,5 trimethylbenzene (mesitylene) had to take into account the relatively high volatility and low solubility of the compound. In order to check if any losses occurred during the mixing of the initial solution, the bottle fill-up, the mixing in the tumbler, the carbon removal procedure or during any transfer step, blank runs of each isolated steps were performed. Initially, both mesitylene and p-xylene were checked because it was not yet determined which compound would be used to test the carbons; p-xylene is more soluble in water although also more volatile than mesitylene.

A.4.1 Determination of losses during mixing in the rotary tumbler

Stock solutions of mesitylene and p-xylene (1000 mg/L) were prepared in distilled methanol. Eighteen bottles were filled with 1 L deionized water. Nine bottles were spiked with 10 mL stock mesitylene solution and similarly nine bottles were spiked with 10 mL stock p-xylene solution. Each bottle was sealed with Teflon tape around the caps and mixed by hand. Eight bottles of each compound were placed in the mixer, while the concentration of the ninth was measured immediately by GC-FID, to determine the initial concentration. A two-point calibration was completed beforehand. The concentration of the bottles placed in the mixer was measured at two-days intervals, two bottles of each compound removed each time. Daily, the GC was rapidly recalibrated. Variations in concentration were observed due to the rapid calibration performed. However, no decreasing trend was detected (see Table A.4.1).

A.4.2 Determination of losses during bottle fill-up

A 20 L glass carboy was filled with approximately 15 litres of deionized water spiked with 150 mL 1000 mg/L stock solution of p-xylene. The carboy was closed to the atmosphere with a rubber stopper. The solution was then pumped into 1 L bottles. Three 1 L samples were taken every four litres and their concentration analyzed by GC-FID (Exp.1). This experiment was then repeated with the stopper tilted so to maintain atmospheric pressure. If the container is kept closed, a vacuum is created as the solution is pumped out, which can modify the gas-liquid equilibrium of the solution. A larger magnetic stirrer was also used to improve the mixing (Exp.2). The results of these two experiments indicate that the modifications brought about improved the consistency of the measured concentrations (see Table A.4.2). Mesitylene was then tested, as with Exp.2, but with a mixing time of 45 minutes to ensure that homogeneity of the solution was achieved. The results show a 2% relative standard deviation between the concentrations of the samples. This error would

Table A.4.1 Losses during mixing in the rotary tumbler

	p-xylene		mesitylene	
Time (days)	Residual conc. (mg/L)	Loss (%)	Residual conc. (mg/L)	Loss (%)
0	10.3		11.5	
2	11.9	+15	11.8	+2.6
	10.1	-1.9	7.1	-38
4	10.7	+3.9	10.6	-7.8
	10.7	+3.9	9.8	-15
7	10.9	+5.8	12.4	+7.8
	10.7	+3.9	12.6	+9.6

be picked-up in the isotherm experiment with the three blanks taken at interval during bottle fill-up.

A.4.3 Determination of losses during filtration

The initial procedure included filtration as a means to remove the carbon particles from the water. In this experiment, to verify if losses were incurred during filtration, six bottles were filled with 1 L water then spiked with 10 mL 1000 mg/L p-xylene. The bottles were inverted by hand 20 times. One bottle was analyzed by GC-FID in duplicate to determine the initial concentration. The other bottles were filtered through glass fiber filter (Whatman 934 AH) and a 15 mL filtrate sample collected. To determine if the filter media adsorbed some of the solute, five volumes of filtrate were discarded: 0 mL, 50 mL, 100 mL, 200 mL and 500 mL. These volumes were roughly measured with a graduated beaker. The results of this experiment with p-xylene and with mesitylene are compiled in Table A.4.3. For each compound, no trend was detected. However, concentrations of mesitylene were significantly lower than for p-xylene. Although a 100 mL discard volume resulted in the lowest losses, it was argued that losses by volatilization of the compounds could not be controlled when filtration was performed, since they were a function of the duration of exposure to the atmosphere.

Table A.4.2 Losses during bottle fill-up

Sample	Concentration (mg/L)	Std. dev. (%)
Exp.1 p-xylene	7.6 6.1 7.6	12
Exp.2 p-xylene	8.9 8.6 8.9 9.2	2.8
mesitylene	9.8 9.6 10.0	2.1

Table A.4.3 Losses during filtration

Sample	Filtrate discarded (ml)	Concentration (mg/L)	Loss (%)
p-xylene blank		6.6	
p-xylene	0	6.3	4.5
	50	5.8	12
	100	6.4	3.1
	200	6.1	7.6
	500	5.5	17
mesitylene blank		9.2	
mesitylene	0	6.9	25
	50	6.9	25
	100	7.5	19
	200	6.9	25
	500	6.6	28

A.4.4 Determination of losses during centrifugation

As an alternative to filtration, centrifugation of the mixture to remove the carbon particles, was investigated. The losses incurred during the centrifugation step were measured. One litre samples of 10 mg/L mesitylene were prepared from a 12 L batch of deionized water spiked with mesitylene. The initial concentration (area count) of each bottle was determined by GC-FID. 50 mL centrifuge tubes were then filled with the samples, until they overflow, to minimize headspace. The screw cap tubes were centrifuged for 20 minutes and then rapidly analyzed to determine the residual concentration. The results are shown in Table A.4.4. Initially, the concentration in the tube prior to centrifugation was measured to check if losses occured by pouring the solution in the tubes (samples 1 and 2). However, to simulate more closely the actual procedure, a recovery check was performed by measuring only the concentration after centrifugation (samples 3 to 8). Recoveries ranged from 83.1% to 99.7%, compared with 72 to 80% with the filtration procedure.

Table A.4.4 Losses during centrifugation

Sample	Initial conc. (area count)	Pre-centrif. conc. (area count)	Pre-centrif. conc. Loss (%)	Post-centrif. conc. (area count)	Post-centrif. conc. Loss(%)	Recovery (%)
1	116 150	111 470	-4.0	107 200	-3.8	92.3
2	117 080	124 610	+6.4	116 780	-6.3	99.7
3	119 470			117 650	-1.5	98.5
4	121 450			100 800	-16.9	83.1
5	128 260			112 320	-12.4	87.6
6	121 990			115 300	-5.5	94.5
7	120 350			114 150	-5.2	94.8
8	129 830			122 950	-5.3	94.7

APPENDIX 5. Raw Data

- Particle size analysis
- Iodine number test
- Tannic acid initial isotherms
- Tannic acid repeat isotherms
- Modified phenol value isotherms
- Phenol in deionized water isotherms
- Phenol in river water isotherms
- Mesitylene isotherms
- TOC isotherms

Table A.5.1 Particle size analysis

PAC	Mass tested (g)	Mass retained on #100 (g)	Mass retained on #200 (g)	Mass retained on #325 (g)	Mass retained on pan (g)	Total mass retained (g)	Loss (%)
Aqua Nuchar	96.0	-0.3	0.3	11.3	82.2	93.8	2.3
Aqua Pac	104.2	0.0	0.1	8.7	93.8	102.6	1.5
WPH	97.7	-0.1	0.1	5.6	91.4	97.1	0.6
WPL	100.1	0.0	0.1	4.6	92.3	97.0	3.1
Watercarb	50.8	0.3	1.1	2.6	46.2	50.2	1.2
Watercarb Plus	82.7	0.5	2.2	20.1	59.7	82.5	0.2
Darco S-51	70.6	0.6	10.4	18.6	38.9	68.5	3.0
Hydrodarco B	73.9	0.0	0.4	6.8	65.7	72.9	1.4
WTC	73.5	9.2	6.8	9.7	45.4	71.1	3.3
PAC 20B	71.3	5.1	11.9	14.1	39.6	70.7	0.8

Table A.5.2 Iodine number test

PAC	Mass tested (g)	Titrant normality	Initial normality	Residual normality	Correction factor	Iodine number
Aqua Nuchar	1.010	0.106	0.0996	0.0266	0.9563	845
	1.011			0.0269	0.9538	838
	1.013			0.0266	0.9563	843
Aqua Pac	1.023	0.106	0.0996	0.0398	NA	
	1.026			0.0397	NA	
	1.042			0.0389	NA	
	1.501			0.0216	0.9888	634
WPH	1.043	0.105	0.0989	0.0291	0.9425	767
	1.001			0.0310	0.9333	767
	1.109			0.0258	0.9606	775
WPL	1.060	0.105	0.0989	0.0277	0.9500	779
	1.095			0.0260	0.9600	782
	1.032			0.0289	0.9438	779
Watercarb	1.009	0.105	0.0989	0.0398	NA	
	1.423			0.0248	0.9663	617
	1.469			0.0227	0.9813	627
	1.437			0.0233	0.9763	632
Watercarb Plus	1.204	0.105	0.0989	0.0286	0.9450	672
	1.206			0.0283	0.9463	675
	1.241			0.0268	0.9550	678

Table A.5.2 Iodine number test, continued

PAC	Mass tested (g)	Titrant normality	Initial normality	Residual normality	Correction factor	Iodine number
Darco S-51	1.517	0.105	0.0992	0.0254	0.9625	574
	1.458			0.0263	0.9575	586
	1.496			0.0257	0.9613	578
Hydrodarco B	1.779	0.105	0.0978	0.0278	0.9500	456
	1.684			0.0295	0.9400	463
	1.695			0.0294	0.9413	461
Norit W-20	1.532	0.105	0.0992	0.0466	NA	
	1.984			0.0172	1.0275	527
	1.789			0.0222	0.9850	523
	1.802		0.0978	0.0204	0.9975	529
WTC	1.500	0.105	0.0978	0.0428	NA	
	1.798			0.0345	NA	
	2.024			0.0296	0.9400	385
PAC 20B	1.906	0.105	0.0978	0.0027	NA	
	1.009			0.0231	0.9775	890
	1.008			0.0234	0.9763	885
	1.023			0.0245	0.9688	851

NA: Not Applicable

Table A.5.3 Tannic acid initial isotherms

PAC	Dosage (mg/L)	Residual conc. (mg/L)
Aqua Nuchar	0	19.9
	50.1	14.9
	100	10.6
	200	4.48
	300	1.70
	401	0.79
Aqua Pac	0	20.0
	50.1	18.8
	100	17.8
	201	15.8
	300	14.7
	400	11.8
WPH	0	20.0
	50.0	17.3
	101	14.5
	200	9.56
	301	6.16
	400	3.37
WPL	0	20.2
	50.0	17.5
	101	15.0
	200	10.1
	301	7.17
	401	3.55
Watercarb	0	19.5
	53.3	18.1
	103	16.9
	200	14.3
	302	12.0
	400	9.75
Watercarb Plus	0	21.1
	50.8	19.4
	101	17.7
	202	14.5
	301	11.6
	400	8.89

Table A.5.3 Tannic acid initial isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Darco S-51	0	20.2
	50.5	14.7
	100	10.2
	201	3.69
	300	1.26
	401	0.64
Hydrodarco B	0	20.2
	50.0	14.2
	101	9.06
	200	3.42
	301	1.90
	400	1.67
Norit W-20	0	20.1
	50.1	18.9
	100	16.9
	201	13.7
	300	10.2
	401	7.56
WTC	0	20.0
	50.2	19.1
	101	17.5
	201	15.3
	300	13.0
	401	11.1
PAC 20B	0	20.1
	50.5	19.6
	101	18.4
	201	16.5
	300	14.2
	401	12.1

Table A.5.4 Tannic acid repeat isotherms

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Aqua Pac	0	19.7
	250	14.8
	501	9.63
	750	5.86
	1000	3.45
	1500	1.58
WPH	0	19.6
	101	14.5
	201	9.70
	299	6.21
	401	3.57
	501	2.24
WPL	0	19.3
	100	14.5
	201	9.68
	300	5.96
	400	3.30
	501	1.97
Watercarb	0	20.0
	251	14.6
	501	8.35
	750	4.21
	1000	1.90
	1500	0.76
Watercarb Plus	0	20.2
	100	17.3
	201	14.4
	350	9.78
	500	7.04
	750	2.34
Norit W-20	0	19.6
	100	16.4
	251	11.3
	500	5.05
	752	2.24
	1000	1.63

Table A.5.4 Tannic acid repeat isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
WTC	0	19.6
	250	13.8
	500	9.26
	753	4.98
	1000	2.93
	1250	1.92
PAC 20B	0	19.8
	102	18.2
	250	14.7
	500	9.46
	752	5.84
	1000	4.16

Table A.5.5 Modified phenol value isotherms

PAC	Dosages (g/L)	Residual conc. (mg/L)
WPH	0	200
	1.53	43.3
	2.00	23.5
	2.56	10.3
	2.98	6.08
	3.50	3.01
WPL	0	200
	1.54	42.3
	1.98	22.2
	2.51	10.0
	3.05	4.71
	3.56	3.01
Aqua Nuchar	0	200
	1.60	69.8
	2.02	48.8
	2.51	32.6
	3.00	21.9
	3.45	15.4
Watercarb	0	200
	1.50	45.4
	2.08	16.1
	2.56	7.20
	3.00	4.25
	3.51	2.56
Hydrodarco B	0	200
	1.48	112
	2.09	77.1
	2.49	59.7
	3.02	41.2
	3.49	29.9
Darco S-51	0	200
	1.48	89.5
	2.09	57.7
	2.50	41.8
	2.96	27.5
	3.49	17.8

Table A.5.6 Phenol in deionized water isotherms

PAC	Dosages (mg/L)	Residual conc. (mg/L)
WPH	0	8.5
	25.0	6.7
	51.8	4.8
	76.2	3.5
	101	2.3
	150	1.1
	202	0.28
	501	ND
WPL	0	8.7
	25.0	5.7
	50.0	4.7
	77.5	3.2
	102	2.2
	152	0.77
	201	0.13
	502	ND
Aqua Nuchar	0	9.0
	24.4	6.9
	52.5	5.9
	80.6	5.0
	101	4.1
	149	2.9
	205	2.0
	501	ND
Watercarb	0	7.4
	25.6	5.5
	53.1	3.9
	80.6	2.2
	100	1.8
	149	0.27
	208	ND
	504	ND

ND: Not detected

Table A.5.6 Phenol in deionized water isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Hydrodarco B	0	8.2
	24.4	7.1
	52.5	5.9
	78.4	5.1
	106	4.4
	151	2.9
	200	2.0
	504	ND
Darco S-51	0	7.5
	30.0	6.3
	50.6	5.3
	75.6	4.8
	102	3.8
	145	2.5
	217	1.3
	497	ND

Table A.5.7 Phenol in river water isotherms

PAC	Dosages (mg/L)	Residual conc. (mg/L)
WPH	0	5.5
	25.0	6.1
	52.5	4.0
	75.0	2.5
	101	0.94
	149	0.37
	222	ND
	504	ND
WPL	0	7.1
	25.6	5.0
	53.7	4.2
	77.5	2.0
	100	1.2
	153	0.24
	201	0.13
	505	ND
Aqua Nuchar	0	5.9
	26.9	6.8
	48.7	4.9
	81.2	3.7
	108	2.7
	151	NM
	202	0.95
	496	0.31
Watercarb	0	6.8
	25.6	5.5
	49.4	3.2
	75.0	2.4
	100	0.96
	154	ND
	208	0.09
	502	ND

ND: not detected
NM: not measured; overflow during fill-up

Table A.5.7 Phenol in river water isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Hydrodarco B	0	7.6
	26.2	7.9
	58.1	7.1
	80.6	6.2
	102	NM
	158	3.5
	201	2.7
	501	0.42
Darco S-51	0	7.2
	28.1	7.3
	52.5	6.3
	86.9	4.6
	106	4.8
	161	2.7
	207	1.7
	507	0.16

Table A.5.8 Mesitylene isotherms

PAC	Dosages (mg/L)	Residual conc. (mg/L)
WPH	0	7.0
	4.98	5.1
	9.96	5.3
	15.0	4.1
	19.7	3.4
	25.1	2.7
	29.8	1.9
	40.5	0.49
	50.0	0.37
	75.2	ND
WPL	0	7.1
	4.79	6.0
	9.96	5.2
	15.0	4.4
	20.1	3.4
	25.1	2.7
	30.1	1.5
	40.4	0.42
	49.8	0.28
	75.0	ND
Aqua Nuchar	0	8.5
	4.61	7.1
	9.96	6.4
	15.0	4.9
	20.1	4.7
	25.3	3.9
	30.3	3.7
	40.1	2.8
	50.3	2.0
	73.4	0.95

ND: not detected

Table A.5.8 Mesitylene isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Watercarb	0	9.6
	5.17	9.0
	9.77	7.3
	15.0	6.1
	19.9	5.6
	25.2	5.9
	29.9	4.9
	40.3	3.9
	50.1	3.0
	75.0	1.3
Hydrodarco B	0	7.6
	4.70	6.6
	10.3	6.2
	15.6	5.3
	20.4	4.7
	25.2	4.3
	30.0	3.9
	39.9	2.9
	50.2	2.2
	75.2	1.2
Darco S-51	0	8.2
	5.08	7.6
	10.1	6.7
	15.1	5.8
	20.2	5.2
	24.8	4.8
	30.0	4.4
	40.7	3.1
	50.2	2.5
	75.2	0.96

Table A.5.9 TOC isotherms

PAC	Dosages (mg/L)	Residual conc. (mg/L)
WPH	0	8.6
	15.1	7.86
	25.2	7.7
	34.9	7.3
	50.0	8.0
	74.9	6.3
	100	5.8
	250	4.0
	500	2.3
	1000	2.1
WPL	0	8.2
	15.0	7.5
	25.0	7.7
	35.0	7.3
	49.9	7.0
	74.9	6.3
	100	5.6
	250	3.8
	500	10.5
	1000	1.8
Aqua Nuchar	0	8.6
	15.0	7.1
	25.0	5.7
	35.1	6.2
	50.3	6.2
	75.0	10.2
	100	4.6
	250	3.1
	500	4.0
	1000	1.5

Table A.5.9 TOC isotherms, continued

PAC	Dosages (mg/L)	Residual conc. (mg/L)
Watercarb	0	7.7
	15.1	7.3
	25.3	7.3
	35.2	7.5
	50.1	17.6
	75.0	6.6
	99.9	6.3
	250	4.7
	500	3.0
	1000	1.6
Hydrodarco B	0	7.5
	14.9	7.1
	25.1	6.8
	34.9	6.3
	49.8	5.7
	75.0	4.5
	99.9	4.3
	250	2.4
	500	5.8
	1000	2.3
Darco S-51	0	8.3
	14.9	7.4
	25.3	8.1
	35.1	5.9
	50.1	7.0
	75.0	4.4
	99.9	2.1
	250	7.1
	500	2.1
	1000	3.4

APPENDIX 6. Calculations

- Particle size distribution
- Iodine number
- Tannin value
- Modified phenol value

A.6 CALCULATIONS

A.6.1. Particle size distribution

$$\%\ \text{Wgt passing \#100 sieve} = \frac{(\text{Wgt}_{200} + \text{Wgt}_{325} + \text{Wgt}_{pan})}{\text{Wgt}_{total}} \times 100$$

$$\%\ \text{Wgt passing \#200 sieve} = \frac{(\text{Wgt}_{325} + \text{Wgt}_{pan})}{\text{Wgt}_{total}} \times 100$$

$$\%\ \text{Wgt passing \#325 sieve} = \frac{\text{Wgt}_{pan}}{\text{Wgt}_{total}} \times 100$$

$$\%\text{loss} = \frac{(\text{Wgt of sample before sieving} - \text{Wgt}_{total})}{\text{Wgt}_{total}} \times 100$$

where: Wgt_{325}: weight retained on #325 sieve

Wgt_{200}: weight retained on #200 sieve

Wgt_{100}: weight retained on #100 sieve

Wgt_{pan}: weight retained on pan

Wgt_{total}: total weight retained on all sieves

<u>Sample Calculations</u>:

PAC: Aqua Nuchar

% Wgt passing #100 sieve =

$$\frac{(0.3 + 11.3 + 82.2)}{93.8} \times 100 = 100\ \%$$

% Wgt passing #200 sieve =

$$\frac{(11.3 + 82.2)}{93.8} \times 100 = 99.7\ \%$$

% Wgt passing #325 sieve =

$$\frac{82.2}{93.8} \times 100 = 87.6\ \%$$

$$\% \text{ Loss} = \frac{(96.0 - 93.8)}{96.0} \times 100 = 2.39 \%$$

A.6.2 Iodine number

Iodine number: Mass of iodine adsorbed per gram activated carbon at a residual iodine concentration of 0.02N.

General equation:

$$\text{Iodine number} = \frac{\text{Iodine adsorbed}}{\text{g PAC}} \times \text{Correction Factor}$$

$$= \frac{X}{M} \qquad * \qquad A$$

$$\text{i) } \frac{X}{M} = \frac{\text{Initial mass iodine} - \text{Residual mass iodine}}{\text{mass PAC}}$$

Initi[illegible]odine = $N_s \times V_i \times \text{E.Wgt.}$

Residual mass iodine = $N_r \times V_i \times \text{E.Wgt.}$

where: N_s: standard iodine solution normality (eq/L)

$$= \frac{Na_2S_2O_3 \text{ normality } \times \text{ mLs } Na_2S_2O_3 \text{ used}}{25 \text{ mL iodine titrated}}$$

N_r: residual iodine filtrate normality (eq/L)

$$= \frac{Na_2S_2O_3 \text{ normality } \times \text{ mLs } Na_2S_2O_3 \text{ used}}{50 \text{ mL iodine titrated}}$$

V_i: volume iodine contacted: 100 mL

E.Wgt.: iodine equivalent weight: 126.91 g/eq

$$\text{ii) A: Correction Factor} = \frac{0.02N^m}{N_r^{\,m}}$$

where: m: slope of an assumed isotherm line, constant.

Values for the correction factor need not be calculated; they are compiled in the AWWA B600-78 Standard.

Equation presented in the AWWA Standard:

Iodine number $= \frac{X}{M} \times A$

$$\frac{X}{M} = \frac{(N_1 \times 12\,693 - 2.2 \times N_2 \times 126.93) \times \text{mL } Na_2S_2O_3 \text{ used}}{\text{Wgt of sample (g)}}$$

where: A: correction factor function of the residual filtrate normality

N_1: normality of iodine solution

N_2: normality of thiosulfate solution

Residual filtrate normality $= \frac{N_2 \times \text{mls } Na_2S_2O_3 \text{ used}}{50 \text{ mL}}$

Rearranging and developing this equation:

$$\frac{X}{M} = \frac{(N_1 \times 126.93 \times 100 \text{ mL}) - (N_2 \times \text{ml } Na_2S_2O_3 \times 126.93 \times 110 \text{ mL})}{\text{wgt of sample} \times 50 \text{ mL}}$$

$$= \frac{\text{(initial mass iodine - residual mass iodine)}}{\text{g PAC}}$$

notes: 1) In the AWWA equations, an equivalent weight [illegible] 126.93 was used for iodine instead of 126.905.

2) A factor of 2.2 (110 mL/50 mL) was used rather than 2.0 (100 mL/50mL).

Sample Calculations (AWWA equation):

PAC: Aqua Nuchar

$$\frac{X}{M} = \frac{(0.0996 \times 12693) - (2.2 \times 0.106 \times 126.93) \times 12.56 \text{ mL}}{1.010 \text{ g}}$$

$= 884$ mg/g

Residual filtrate normality $= \frac{0.106N \times 12.56 \text{ mL}}{50 \text{ mL}} = 0.0266N$

From Table 1 in the AWWA B600-78 Standard:
for a residual filtrate of 0.0266N, A = 0.9563

∴ Iodine number = 884 x 0.9563 = 845 mg/g

A.6.3. Tannin value

Tannin value: Dosage of activated carbon required to reduce a 20 mg/L tannic acid solution to 2 mg/L.

$$\text{Carbon loading} = q_e = \frac{(C_o - C_e)}{M}$$

$$\therefore \text{Tannin value} = M = \frac{(C_o - 2\ \text{mg/l})}{(q_e \text{ at } C_e = 2\ \text{mg/l})}$$

where: q_e: carbon loading determined from the isotherm regression line (mg/mg)

C_o: initial tannic acid concentration, determined from blank (mg/L)

C_e: residual tannic acid concentration (mg/L)

M: carbon dosage: tannin value (mg/L)

Sample calculations:

PAC: Aqua Nuchar

isotherm equation: $\log q_e = \log(0.0521) + 0.254 \log C_e$

at $C_e = 2$ mg/L, $\log q_e = -1.21$

$$\text{Tannin value: } M = \frac{(19.9\ \text{mg/L} - 2\ \text{mg/L})}{\log^{-1}(-1.21)} = 290\ \text{mg/L}$$

A.6.4. Modified phenol value

Modified phenol value: Dosage of activated carbon required to achieve a 90 % removal of phenol from a 200 mg/L solution.

$$\% \text{ Carbon loading} = \% q_e = \frac{\frac{(C_o - C_e)}{C_o} \times 100}{M}$$

$$\therefore \text{Modified phenol value: } M = \frac{90\ \%}{\% q_e \text{ at } \% C_e = 10\ \%}$$

where: C_e: residual phenol concentration (mg/L)

$\% C_e = \frac{C_e}{C_o} \times 100$

C_o: initial phenol concentration determined from blank (mg/L)

$\% q_e$: carbon loading determined from the isotherm regression line (%/g/L)

M: carbon dosage: modified phenol value (g/L)

Sample calculations:

PAC: Aqua Nuchar

Isotherm equation: $\log q_e = \log(25.6) + 0.223 \cdot \log C_e$

at $C_e = 10\ \%$, $\log q_e = 1.63$

$$\therefore \text{Modified phenol value: } M = \frac{90\ \%}{\log^{-1}(1.63)} = 2.10 \text{ g/L}$$

APPENDIX 7. Mesitylene Individual Isotherms

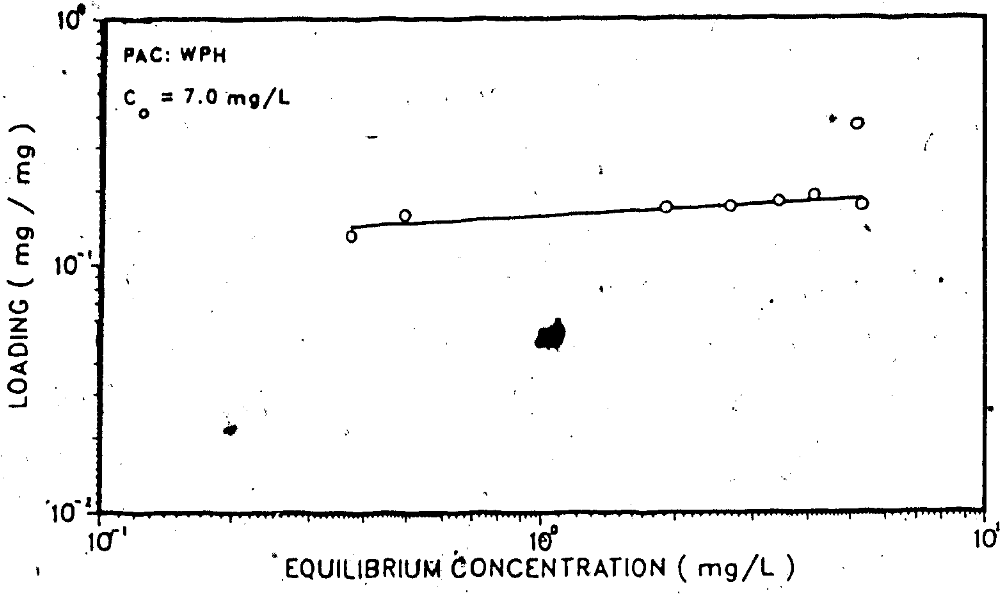

Figure A.7[illegible] - Mesitylene isotherms

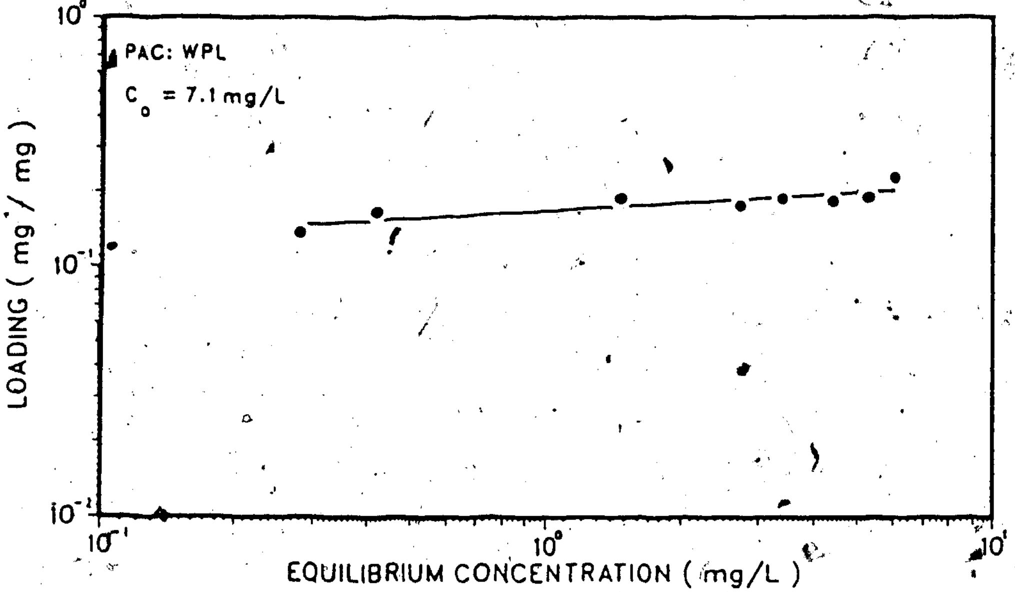

Figure A.7.2 WPL - Mesitylene isotherms

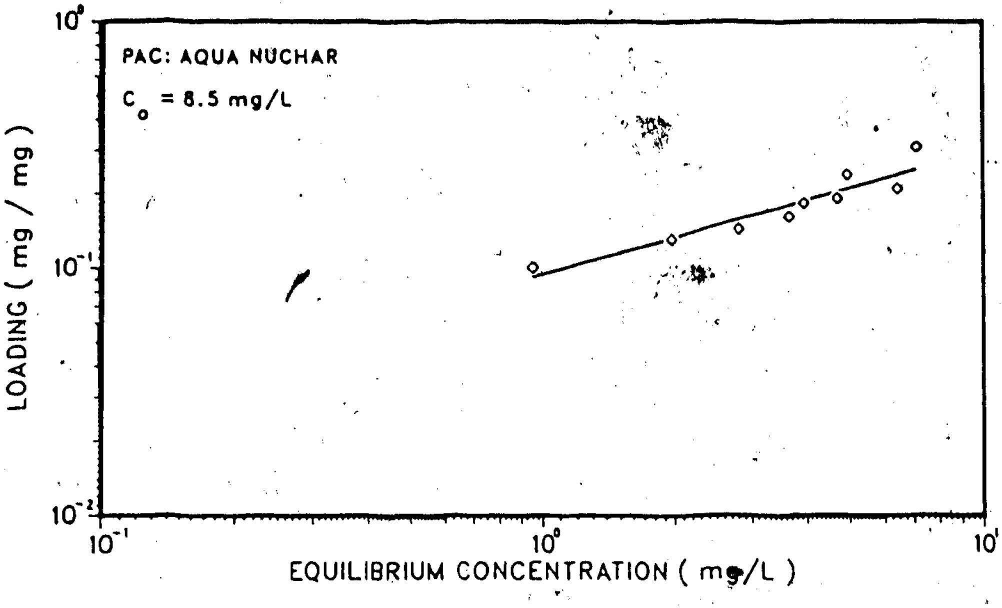

Figure A.7.3 Aqua Nuchar - Mesitylene isotherms

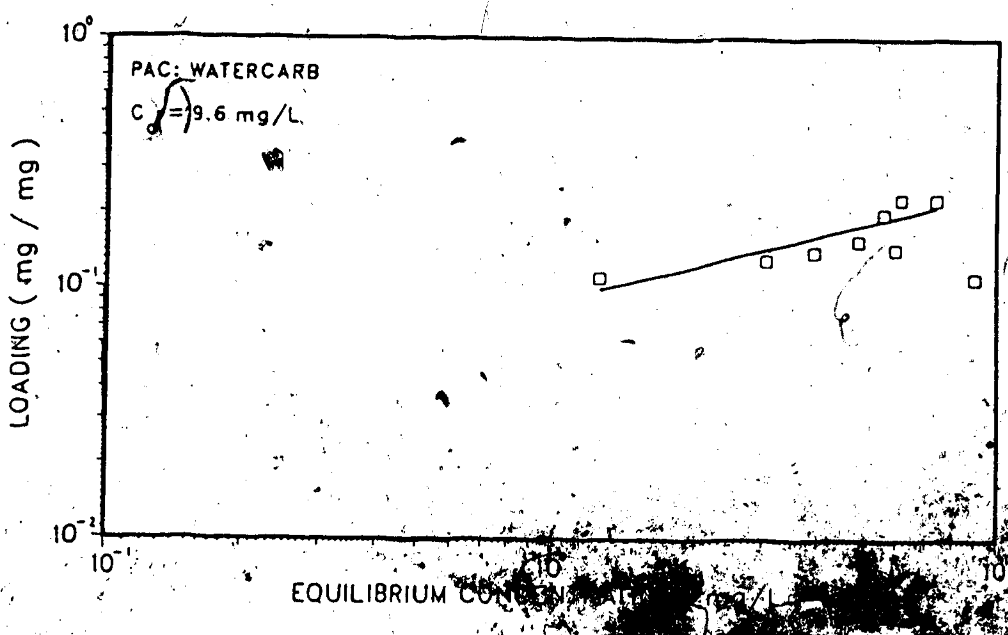

Figure A.7.4 Watercarb - Mesitylene isoterms

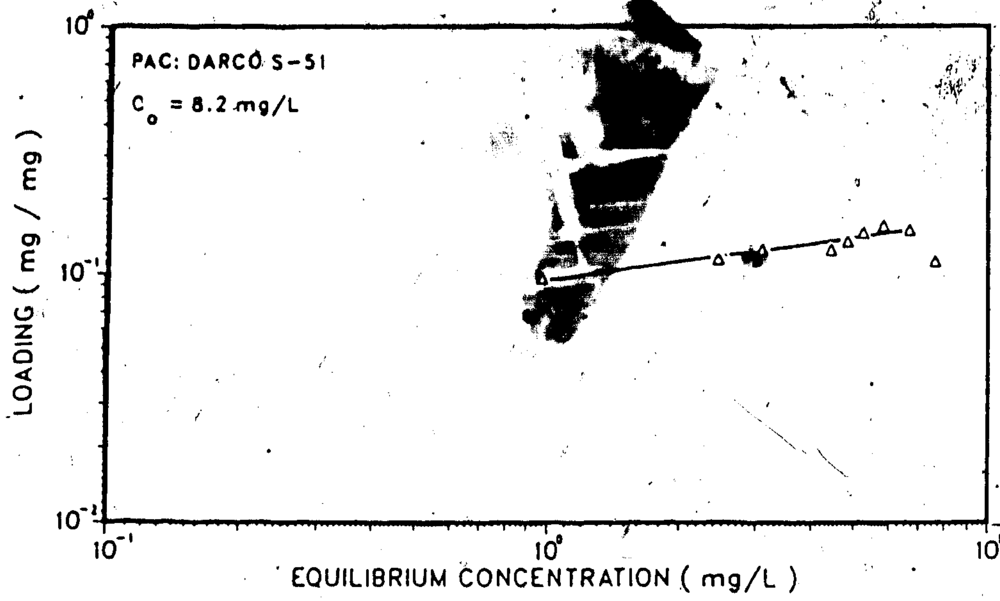

Figure A.7.5 Darco S-51 - Mesitylene isotherms

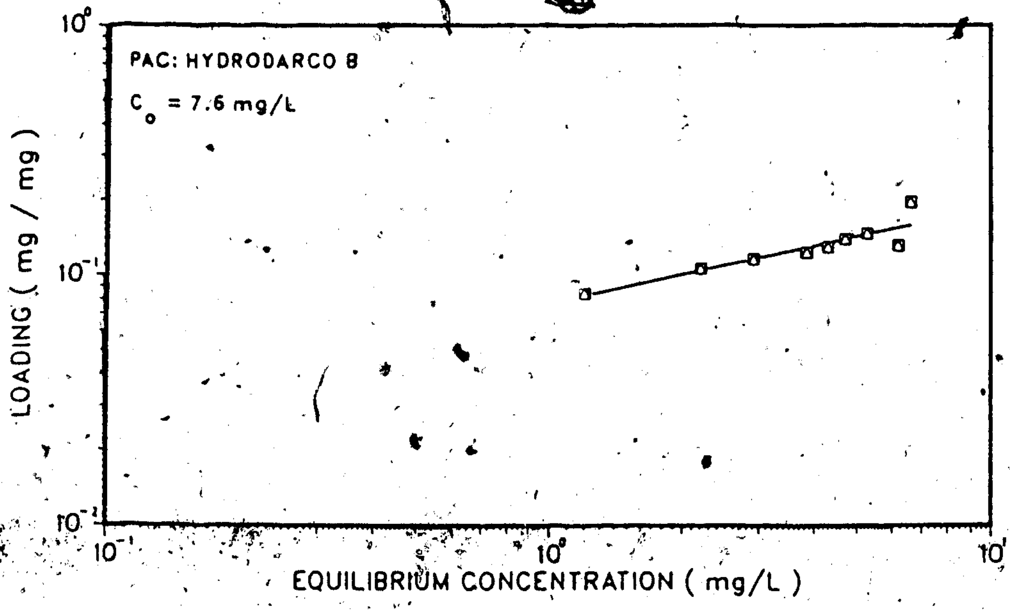

Figure A.7.6 Hydrodarco B - Mesitylene isotherms

APPENDIX 8. Selection Procedure for PAC in Edmonton

A.8 SELECTION PROCEDURE FOR PAC AT THE EDMONTON WATER TREATMENT PLANTS, FEBRUARY 1987

The City of Edmonton purchased 650 tonnes of powdered activated carbon for the Rossdale and E.L. Smith Water Treatment Plants in February 1987. The PAC was selected on the basis of the AWWA specifications and its "evaluated price". The selection and purchase procedure used by the City of Edmonton is summarized in this Appendix.

Firstly, the acceptable tenders had to include:

- an affidavit of compliance with the AWWA B600-78 Standard for PAC;
- a reference sample with a certified test report which shows compliance with the requirements of the specifications, on the basis of: moisture content, apparent density, particle size distribution, iodine number, modified phenol value and tannin value;
- an acceptance letter for the sampling procedures.

The reference samples were tested and the PACs which satisfied the minimum requirements provided in the AWWA B600-78 Standard were evaluated using a simple algorithm. In this formula, the PACs are graded by comparison to chosen optima standard test values. In addition, a "weight factor" has been assigned to each standard test. The upper limit of the range of standard test values expected for water treatment PACs was used as the optimum value for comparison and grading. For the iodine number test, the modified phenol value test, and the tannin value test, these upper limits correspond to 1000 mg/g, 2.0 g/L and 200 mg/L, respectively. The "weight factors" were chosen on the assumption that PAC is applied to adsorb low molecular weight compounds. Therefore, more weight was assigned to the iodine number and modified phenol value than on the tannin value. The resulting "evaluation factor" was calculated as follows:

$$\text{Evaluation Factor} = 0.4 \times \frac{\text{Iodine number}}{1000} + 0.5 \times \frac{2.0}{\text{Modified phenol value}} + 0.1 \times \frac{200}{\text{Tannin value}}$$

The highest evaluation factors were considered for selection.

The evaluated price was then determined as follows:

$$\text{Evaluated price} = \frac{\text{Bid unit price (\$/ton)}}{\text{Evaluation factor}}$$

The bid with the lowest evaluated price was selected.

With each load delivered from a fresh batch, the vendor had to supply a certificate of analysis indicating that the PAC was of equal quality to the reference sample provided with the tender documents. To control the quality of the material delivered, the City of Edmonton sampled the shipments of PAC and verified their compliance to the AWWA Standard.

APPENDIX 9. Diagram of Rotary Tumbler

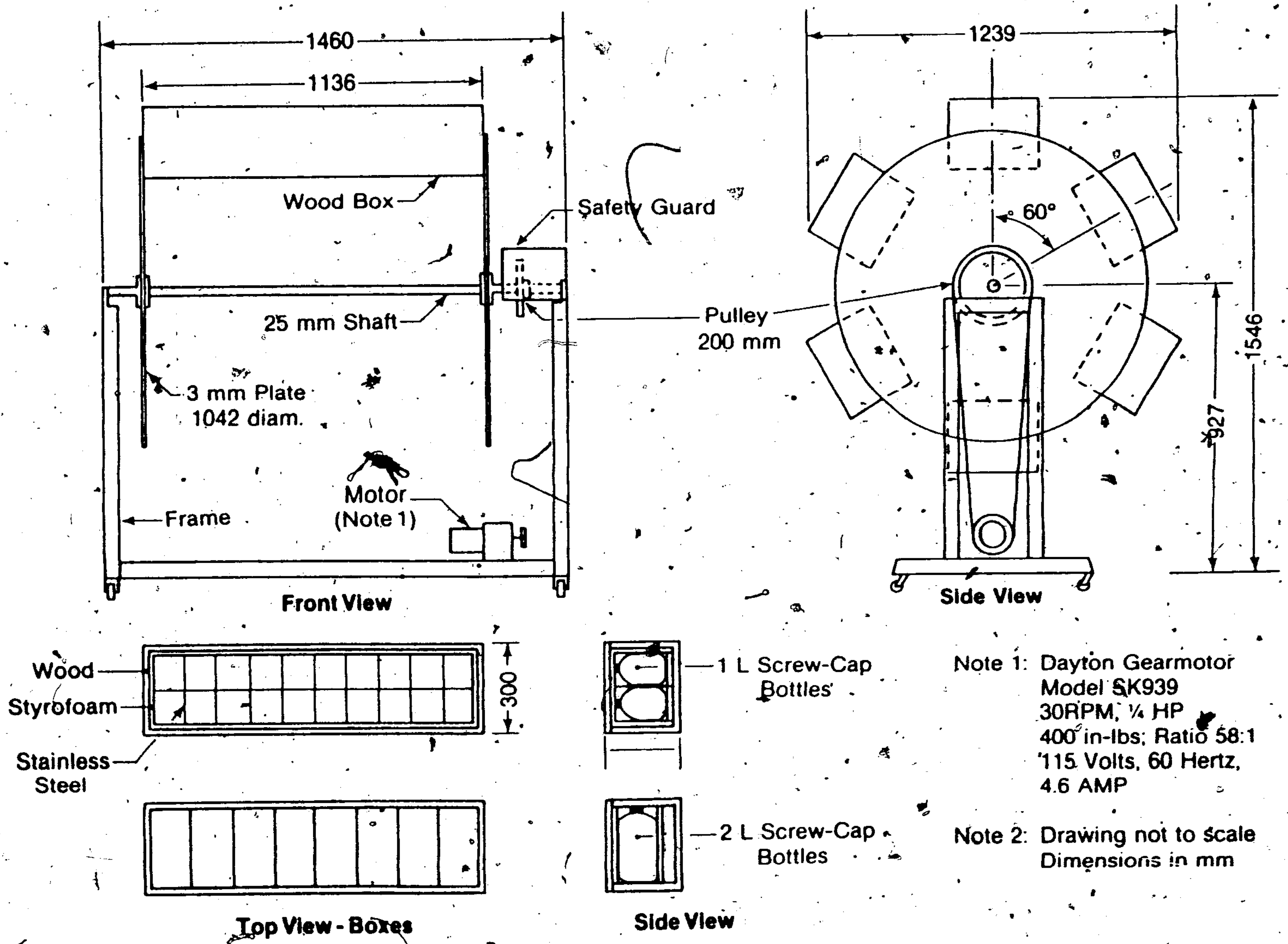

Figure A.9 Diagram - Rotary tumbler (for 1L and 2L bottles)