

**EVALUATION OF POWDERED ACTIVATED
CARBON (PAC) FOR THE REMOVAL OF TASTE AND
ODOUR CAUSING COMPOUNDS FROM WATER AND
THE RELATIONSHIP BETWEEN THIS
PHENOMENON AND THE PHYSICO-CHEMICAL
PROPERTIES OF THE PAC AND THE ROLE OF
WATER QUALITY**

**Final Report
to the
Water Research Commission**

by

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EXECUTIVE SUMMARY

The quality of surface waters in South Africa is deteriorating as a result of human activities such as agriculture, industry and runoff from habitations where sanitation is either of a poor standard or even non-existent. Eutrophication as a result of the organic enrichment of the water in impoundments leads to the establishment and proliferation of organisms which may release toxins and taste and odour forming substances into the water. Two of the most common taste and odour compounds are geosmin and 2-methylisoborneol (2-MIB).

Most waterworks treating such waters are not equipped to remove the taste and odour substances due to the high cost, the intermittent nature of the problem or an insufficient level of technology.

The most commonly used method of removal of geosmin or 2-MIB from water is the use of activated carbon. This is achieved either by the use of granular activated carbon (GAC) in fixed beds on a continuous basis, or by dosing powdered activated carbon (PAC) into the water on an intermittent basis whenever there is a taste and odour problem at the works. The use of GAC is associated with high capital costs but moderate running costs due to the ability to regenerate the carbon, whereas the use of PAC entails relatively high chemical costs due to the carbon being discarded after use, but is low in capital cost. Because PAC is only used intermittently its overall cost is frequently lower than GAC and it tends to be the preferred method in South Africa.

Activated carbon can be made from a number of feedstocks but most frequently coal, coconut shells, or wood is used. The methods of manufacture and activation also vary and it is important to be able to characterise a carbon in terms of its adsorptive abilities. This has led to a number of empirical measures being developed where the adsorptive ability is expressed in terms of its adsorptive capacity for a particular substance. Examples are iodine number, methylene blue number, and tannin number. These numbers are intended to provide an estimate of the adsorptive capacity of the particular carbon not only for the compound in question but also for other compounds of similar molecular size and configuration.

Unfortunately experience has shown that the commonly used adsorption numbers do not predict the ability of a carbon to adsorb geosmin or 2-MIB. Since the measurement of the performance of a carbon requires detailed investigation and sophisticated equipment and laboratory facilities, such work cannot be readily undertaken by most water treatment authorities or even many suppliers.

This project was initiated with the following objectives in mind:

- To establish the relationship between the physico-chemical properties of PAC for the removal efficiency of taste and odour causing compounds from water.
- To determine what effect water quality and the chemical composition has on the removal of taste and odour by adsorption onto PAC.
- To determine if the same PAC product could be used effectively in all regions throughout South Africa with the aim of setting up a centralised stock to serve more than one water treatment authority.
- To try to establish whether compounds exist which have similar adsorption behaviour by PAC as geosmin, but which are cheaper and easier to evaluate.
- To set guidelines for the evaluation of PAC for the removal of taste and odour causing compounds like geosmin and 2MIB.

Samples of PAC were requested by Rand Water from all interested suppliers in South Africa and of these ten were selected for testing. The physico-chemical properties of the ten PAC samples used in the evaluation were characterised as follows :-

- Moisture content
- Ash content
- Bulk density
- Particle size analysis
- Nitrogen intrusion determinations
- Mercury intrusion determinations
- Tannin number determination
- Iodine number determinations
- Methylene blue number determinations
- Geosmin adsorption determinations

- 2-MIB adsorption determinations

The ability of the various PAC samples to adsorb geosmin and 2-MIB were then compared against the physical characteristics as well as other factors such as the quality of the water and the treatment process employed at the relevant waterworks in an attempt to find good correlations or even the ability to predict a carbon's performance.

It was found that water quality does affect the ability of PAC to adsorb geosmin and 2-MIB with best results being obtained for deionised water and worst results for water containing a relatively high concentration of suspended solids.

Similarly the water treatment process also affected adsorption with lime having little effect, polyelectrolyte having a relatively minor effect, and sodium silicate being significantly inhibitory to geosmin and 2-MIB adsorption.

No significant correlation between adsorptive ability and physical characteristics of the PAC was evident and the adsorption numbers were also not predictive of performance apart from a fairly weak negative correlation between geosmin adsorption and tannin number.

Samples of the five best performing carbons were then sent to two other water treatment authorities (Cape Town Metropolitan Council and Umgeni Water) and submitted to similar tests for Geosmin and 2-MIB adsorption using the individual in-house methods. It was encouraging that the best three carbons were the same for all three authorities in that the methods appeared to be reproducible and the use of a central PAC stockpile became a practical possibility.

A rapid visual assessment method for PAC performance developed by Cape Town Metropolitan Council laboratory using either judgement by eye or absorption at 850 nm on a spectrophotometer was tested. It was found that this was a useful preliminary indicator but not an error free predictor of performance.

The project did therefore not succeed in developing a simple reproducible test for estimating the adsorptive capacity of a PAC for geosmin or 2-MIB although the Cape Town colourimetric estimation method could eliminate some preliminary screening work. Future work is recommended in conjunction with manufacturers to establish whether manufacturing

techniques can be refined to reliably produce good adsorption results for taste and odour substances.

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“Evaluation of Powdered Activated Carbon (PAC) for the removal of taste and odour causing compounds from water and the relationship between this phenomenon and the physico-chemical properties of the PAC and the role of water quality”

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GLOSSARY

AWWA	American Water Works Association
BOM	Background organic matter
DADMAC	Diallyldimethylammoniumchloride
GAC	Granular activated carbon
HSDM	Homogeneous surface diffusion model
IAST	Ideal adsorbed solution theory
2-MIB	2-methylisoborneol
PAC	Powdered activated carbon
SOC	Synthetic organic carbon
TDS	Total dissolved solids
VOC	Volatile organic carbon
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Deteriorating water quality in South Africa as a result of inadequate sanitation, runoff from agricultural lands and discharges of industrial effluents to watercourses, is giving rise to eutrophication of surface water impoundments. Eutrophication leads to an increase in algogenic taste and odour compounds as well as the possibility of algal toxins such as microcystin. The presence of biologically produced taste and odour compounds like geosmin and 2-methylisoborneol (2-MIB) in drinking water often leads to consumer complaints, while toxic compounds like microcystin may go unnoticed.

Very few water treatment plants in South Africa are equipped to remove these problematic organic micropollutants. In most cases, these biologically produced taste and odour compounds result in the water being unpalatable, but are not harmful. Unit treatment processes for the removal of taste and odour compounds and other metabolites are not generally installed for the following reasons:

- the problems normally occur sporadically or seasonally
- there is seldom any associated health risk
- treatment costs are high.

The most commonly used treatment method is the use of activated carbon supplied either as granular activated carbon (GAC) in fixed beds on a continuous basis, or as powdered activated carbon (PAC) dosed intermittently as required. Although the capital cost for the latter process is relatively low, the chemical costs and hence the unit treatment cost, can be high. GAC applied in fixed beds is therefore often more cost effective if the treatment is required for long periods.

PAC is usually only required intermittently and the selection of the correct type of material can present a problem as the water quality may change, thus potentially having an influence

on the efficiency of adsorption of the taste and odour compounds. It is therefore important to establish the possible relationship between the physico-chemical properties of PAC and the ability to remove taste and odour causing compounds from water and also to investigate whether water quality can influence the efficiency. No set of universally acceptable methods for the evaluation of PAC has been proposed and water treatment facilities therefore often have to rely on methods developed in-house, by PAC suppliers, or by outside resources. PAC selection could therefore be based on inadequate or wrong information, which leads to inefficient treatment and economic losses. To date very little knowledge is available on the possible relationship between the physico-chemical properties of PAC and the removal of taste and odour compounds from water. Contrary to situations where the adsorptive capacity of carbon can be characterised by the adsorption of iodine or methylene blue expressed as numbers, it seems as though these indices give little or no indication of the efficiency of adsorption of geosmin or 2-MIB. The reason could be that the physical, chemical and molecular properties of taste and odour compounds differ markedly from those compounds used to measure adsorptive capacity and that different indicators, such as tannin adsorption should receive more attention.

1.2 Objectives

The project was initiated with the following objectives in mind:

- To establish the relationship between the physico-chemical properties of PAC for the removal efficiency of taste and odour causing compounds from water.
- To determine what effect water quality and the chemical composition has on the removal of taste and odour by adsorption into PAC.
- To determine if the same PAC product could be used effectively in other regions in South Africa with the aim of setting up a centralised stock to serve more than one water treatment authority.
- To try to establish whether compounds exist which have similar adsorption behaviour by PAC as geosmin, but which are cheaper and easier to evaluate.
- To set guidelines for the evaluation of PAC for the removal of taste and odour causing compounds like geosmin and 2MIB.

A PAC dosing plant was installed at Rand Water in 1999 and PAC suppliers were subsequently invited to supply representative samples of suitable products for the evaluation

of geosmin and 2-MIB removal. The 10 most cost effective products from the evaluation were used in this project and as a result benefited the project in the following ways:

- The task of sourcing representative samples of suitable products was therefore eliminated.
- Samples were received from a wide range of PAC suppliers and as many samples as possible were therefore considered. Suppliers were limited to two products only.
- The geosmin adsorption isotherms were already available, which resulted in a cost saving for the project due to the high analysis cost of geosmin.

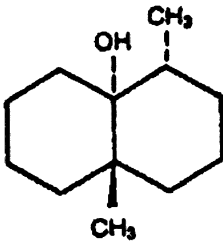
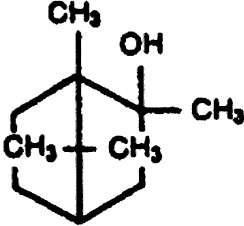
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biologically produced taste and odour problems in drinking water are a common source of customer complaints worldwide. Some species of blue green algae and actinomycetes are capable of producing compounds of distinct odours. Blooms of cyanobacteria (blue-green algae) in particular have been implicated in incidents of earthy/ musty taints in water. Two compounds most commonly detected in water during taste and odour episodes are geosmin (*trans*-1, 10-dimethyl-*trans*-9-decalol) and 2-methylisoborneol (1,2,7,7-tetramethyl-*exo*-bicyclo(2.2.1)heptan-2-ol) (see **Table 1** for molecular structures). Geosmin has a distinct muddy aroma while 2-methylisoborneol (2-MIB) smells like camphor when present in the concentrated form and has a musty aroma when diluted.

Table 1: Properties of two odorous compounds, namely geosmin and 2-MIB.

Compound	Geosmin	2-MIB
Formula	C ₁₂ H ₂₂ O	C ₁₁ H ₂₀ O
Structure		
Boiling point (°C)	270	210

2.2 Removal of Musty-Odoriferous Compounds from Water

The odour threshold concentration of 2-MIB has been reported to be 18-20 ng/l by Person. Four out of a panel of 17 judges and eight out of another panel of 16 judges could discern the

distinctive odour of 2-MIB in the same study. The highest and lowest geosmin concentration measured at consumer taps within Rand Water's distribution area during an odour complaint period (May 1992) was 28 and 10 ng/l respectively. Lalazary *et al.* reported the odour threshold concentrations of 2-MIB and geosmin as 9 and 4 ng/l respectively.

Taste, odour and clarity are parameters estimated and used by the consumer to assess potable water quality as provided by the water authority. The occurrence of taste and odour in potable water supplies could lead to the water being perceived by the consumer to be harmful or toxic. The consumers' concerns can reflect back on the credibility of the water authority and of tap water in general. South Africa has already seen a tremendous growth in the bottled water market, which could be viewed as an indicator of a lack of consumer confidence in potable water quality supplied by water authorities. Water treatment authorities are therefore challenged to remove the taste and odour compounds present in the raw water source to below the threshold odour concentrations to maintain public confidence in water quality. Levels of geosmin concentrations found in the untreated water to purification plants during outbreaks of taste and odour problems at three water authorities in South Africa are summarised in **Table 2**.

Table 2: Geosmin concentrations encountered at Cape Metropolitan Council, Rand Water and Umgeni Water in South Africa [6]

	Cape Metropolitan Council	Rand Water	Umgeni Water
Source/Treatment Plant	Theewaterskloof	Zuikerbosch	Durban Heights (Nagle Dam)
Period	1982-2002	May 1992	March 1994
Minimum (ng/l)	0	14	6
Maximum (ng/l)	170	180	385
Average (ng/l)	70	89	105

The effectiveness of various unit processes and operations to remove taste and odour compounds have been investigated. This includes conventional water purification processes (coagulation, sedimentation and filtration), physical methods (atomic radiation, high energy accelerated electrons, high energy UV light, electrical discharges and air stripping), oxidation (Cl_2 , KMnO_4 , ClO_2 , O_3 and $\text{UV/H}_2\text{O}_2$) and adsorption (activated carbon and resins).

Taste and odour compounds are usually contained in both the water and algal cell bodies. The compounds in the solid phase can be effectively removed through coagulation, sedimentation and filtration. However, conditions that would promote lysis of the algal cells would release the taste and odour compounds into the water phase. The increase in dissolved taste and odour compound concentrations from cell lysis was clearly illustrated by Ando *et al* (1992) in determining the effect of prechlorination on dissolved geosmin and 2-MIB concentrations.

Conventional treatment processes are usually inadequate in removing taste and odour compounds in the water phase to below the odour threshold concentration. This is illustrated in **Table 3** by showing the removal efficiencies of geosmin through a conventional treatment process. Surface water (Vaal Dam) is treated at Rand Water using lime as coagulant (60-80 mg/l as CaO), activated sodium silicate (2,5 mg/l) as coagulant aid and ferric chloride (0,5 mg/l Fe) as secondary flocculant/ filtration aid.

Table 3: Average removal efficiency of purification plants at Rand Water for the period 17 January 1997 to 5 February 1997.

Location	Plant	Geosmin removal efficiency (%)	Geosmin concentration in final water (ng/l)
Vereeniging	1	87	10
	2	70	25
Zuikerbosch	1	85	11
	2	82	13
	3	58	31
	4	67	24

The reasons for the differences in removal efficiencies between the plants are not known. Plants 1 and 2 at Vereeniging and Zuikerbosch have dual sedimentation tanks (horizontal flow) while plants 3 and 4 at Zuikerbosch have a single horizontal flow sedimentation tank. A possible explanation might be offered by the fact that some of the geosmin may be contained in the solid phase and the dual sedimentation systems are more effective in removing suspended matter. Laboratory tests showed that 86% geosmin removal efficiencies ($C_0 = 215$ ng/l) could be obtained using lime/ activated sodium silicate or lime/ ferric chloride as coagulants, which is in broad agreement with the plant data.

Bruce *et. al.* [] investigated the optimisation of alum coagulation for geosmin and 2-MIB removal and found no significant removal over a range of pH and coagulation conditions. This finding is also in agreement with previous research that found coagulation to be ineffective for the removal of geosmin and 2-MIB in the water phase.

Gamma rays and high-speed, high-energy electron treatment was found to be very effective in removing taste and odour compounds from the water. These technologies were not found to be cost-effective and also produce undesirable by-products like nitrite ions in the water.

The removal of five taste and odour compounds by air stripping from water was investigated by Lalezary *et. al.* Henry's law constants were determined for the compounds as Henry's law best expresses the equilibrium between air and water at low concentrations. The Henry's law constant for chloroform was approximately fifty times larger than that of geosmin and 2-MIB. The amounts of geosmin and 2-MIB that can be air-stripped at neutral pH are therefore insignificant, so air-stripping is not a feasible option for the removal of these compounds.

Lalezary *et al.* established the relative order of various oxidants for removing geosmin and 2-MIB efficiently as $\text{ClO}_2 > \text{O}_3 > \text{MnO}_{2(s)} > \text{Cl}_2 > \text{KMnO}_4$ and $\text{ClO}_2 > \text{O}_3 > \text{Cl}_2 > \text{MnO}_{2(s)} > \text{KMnO}_4$ respectively. It was however necessary to use test conditions that were often impractical, including wide ranges of dosages and contact times in order to derive a conclusive ranking of efficiencies. Removal efficiencies of 30% or less were obtained for a practical range of ClO_2 dosages and contact times. High doses of O_3 were effective in reducing geosmin concentrations to less than 10% of the initial concentration. Bruce *et al.* determined that geosmin and 2-MIB could be reduced to 9% and 18% of the initial concentration respectively at an initial O_3 residual of 2,5 mg/l and a contact time of 3 minutes. The presence of hydroxyl scavengers severely impacted on the efficiency of ozone to reduce the geosmin and 2-MIB concentrations to acceptable levels.

Rand Water tested the efficiency of various oxidants and combinations of oxidants to remove geosmin from water and the results are summarised in **Table 4**.

Table 4: Effectiveness of various oxidants to remove geosmin from water as tested by Rand Water [8]

Oxidant	Initial geosmin concentration (ng/l)	Contact time (minutes)	Dosage range	Unit	Removal (%)
Ozone (O ₃)	245	ns	0.85 – 3.12	mg/l	15-46
Hydrogen peroxide (H ₂ O ₂)	350	1	1 – 10	mg/l	3–7
Ultraviolet light (UV light)	379		650 – 2600	mJ.cm ⁻²	11-29
O ₃ and H ₂ O ₂	241	ns	0.85-2.68: 0.43-1.34	mg/l O ₃ : mg/l H ₂ O ₂	21-63
H ₂ O ₂ and UV	342	1	1-3: 490	mg/l: mJ.cm ⁻²	8-20
H ₂ O ₂ and UV	342	1	1-3: 560	mg/l: mJ.cm ⁻²	28–62
H ₂ O ₂ and UV	342	1	1-3: 2600	mg/l: mJ.cm ⁻²	41-69

ns = not specified

Three synthetic resins and activated carbon were tested and compared by Chudyk *et al.* for the removal of 2-MIB. A macroporous phenol-formaldehyde weak base resin showed no absorbing capacity for 2-MIB. The capacity of a styrene-divinylbenzene resin was also significantly lower than that of the low adsorbing activated carbons and regeneration of the resin failed using steam or ethanol. A carbonaceous resin showed the most promise, although this displayed somewhat less adsorbing capacity for 2-MIB than activated carbon. The resin could however not be regenerated satisfactorily with atmospheric steam or ethanol. It was therefore concluded by Chudyk *et al.* that water treatment plants could not use resins for taste and odour removal.

Magnetite exhibits adsorptive properties for suspended and dissolved compounds in water. In the Sirofloc process, fine magnetite is added to water, allowed to adsorb the target matter or compounds and is then removed using a magnet. Successive acid and alkali treatment steps are used to reactivate the magnetite before recycling. A geosmin removal efficiency of 40% was achieved at a dosage of 55 mg/l when tested at Rand Water.

Lalezary *et al.* determined the adsorb abilities of five organics by activated carbon as follows: 2,3,6-trichloroanisole (TCA) > 2-isobutyl-3-methoxypyrazine (IBMP) > 2-isopropyl-3-methoxypyrazine (IPMP) > geosmin > 2-MIB. Moderate PAC dosages (20 mg/l) displayed greater than 90% organics removal. Activated carbon, whether in the powdered or granular

form, has been determined as the most effective single treatment step for taste and odour problems.

2.3 What is Activated Carbon?

The American Water Works Association (AWWA) defines activated carbon as “a family of carbonaceous substances manufactured by processes that develop internal porosity, thereby creating adsorptive properties”. Activated carbon is usually manufactured through the thermal decomposition of carbonaceous material followed by activation with chemicals, steam or carbon dioxide at temperatures between 700 and 1100°C. The tarry carbonisation products that are formed during the pyrolysis processes are essentially removed during the activation process, thereby creating a highly porous product. A wide variety of raw materials (waste tyres, petroleum heavy oil, cellulose, phenol formaldehyde resin, rice husks, pulp mill residue, corn cobs, coffee beans, and bones) can be used, but bituminous coal, anthracite, wood, coconut shell, and lignite are the materials most commonly used.

Activation is achieved by one of two methods namely chemically or thermally. Chemical activation reagents are dehydrating agents, with phosphoric acid being the most popular. Zinc chloride and sulphuric acid are also commonly used, while others, which have been used in the past, include calcium hydroxide, calcium chloride, manganese chloride and sodium hydroxide. Saw dust is usually used as the raw material during chemical activation. Raw material and reagent are mixed into a paste, dried and carbonised at temperatures around 600°C. Further activation with steam at temperatures of 700 to 800°C is sometimes used. The activity is sensitive to the proportion of raw material to reagent, kiln temperature and retention time.

Virtually all materials can be activated thermally, but peat, lignite, bituminous coal, anthracite and coconut shell are among the most common. Different thermal activation methods have been developed, each being appropriate to a particular type of raw material. Generally, carbonisation takes place at temperatures between 500 and 900°C with simultaneous or subsequent activation (steam/ CO₂) at 800 or 900°C. The steam activation process can be self-sustaining in terms of energy since the conversion of carbon to carbon dioxide is exothermic.

The structure of activated carbon consists of elementary microcrystallites of graphite. The porosity of the material is essentially formed by the spaces between the microcrystallites, which are stacked together in a random orientation. The pore size distribution is trimodal, giving rise to micro-, meso- and macropores. The pore size distribution and total pore volume associated with each pore size range is determined by the raw material used, initial pyrolysis and activation procedures. The role that the raw material plays in the properties of the activated carbon is illustrated by comparison of the different products formed using similar methods and degrees of activation, but different raw material sources. The coconut-based products tend to have dense structures consisting of large graphite plates situated close together. The wood-based products have an open structure with smaller graphite plates and many more larger pores, while the coal-based products have a structure somewhere between that of the coconut- and wood-based products. **Table 5** indicates the typical sizes of the micro-, meso- and macropores, while **Table 6** shows the differences between activated carbons produced from various raw material sources.

Table 5: Pore sizes in typical activated carbons.

		Micropores	Mesopores	Macropores
Diameter	nm	< 2	2 to 50	> 50
	Å	< 20	20 - 500	> 500

Table 6: Typical properties of activated carbons produced from various raw material sources (Carbochem).

Property	Coconut	Coal	Lignite	Wood
Micropore	High	High	Medium	Low
Macropore	Low	Low	High	High
Hardness	High	High	Low	Medium
Ash	5%	10%	20%	5%
Water Soluble Ash	High	Low	High	Medium
Dust	Low	Medium	High	Medium
Regeneration	Good	Good	Poor	Fair
Apparent Density	0,48 g/cc	0,48 g/cc	0,3 g/cc	0,35 g/cc
Iodine Number	1 100	1 000	600	1 000

The activation procedures could be adapted to produce activated carbons with even higher porosity and surface area than that displayed in **Table 5**. The activated carbon surface is

essentially non-polar and therefore tends to be hydrophobic and organophilic. Slight polarity may arise from surface oxidation.

Reference has been made in paragraph 2.2 to the different forms of activated carbon, in particular, *powdered* and *granular* activated carbon. These two forms of activated carbon are essentially the same but differ considerably in usage. The two forms can be produced simultaneously or the granular form can be crushed to produce the powder. Activated carbon with a particle size of less than about 0,4 mm is regarded as a poor filtration media and is processed to be marketed as the powdered form. The particle size distribution of PAC has to meet the following specification according to the AWWA: not less than 99% shall pass through a 149 μm aperture sieve, not less than 95% shall pass through a 74 μm aperture sieve, not less than 90% shall pass through a 44 μm aperture sieve. The user can specify coarser material to prevent filtration media penetration by the PAC. PAC is used almost entirely in liquid applications whereas GAC could be applied in gas-phase applications.

PAC and GAC are used at potable water treatment plants to remove organic compounds from water. Categories of these compounds include taste and odour causing compounds, synthetic organic chemicals (SOC), pesticides, herbicides, colour and trihalomethane precursors. PAC has the advantage of being a cheaper material and requiring less capital expenditure for the dosing and mixing equipment. PAC can also be applied when needed and has therefore been the material of choice to treat taste and odour problems that occur for a relatively short of time during the year. GAC is applied in fixed filter beds and has advantages of lower carbon usage rates and re-use of the material through regeneration. GAC has been the adsorbent of choice for removing SOC's, which include volatile organic carbon (VOC).

2.4 Predicting the Capacity of Activated Carbon

Two methods are available to apply activated carbon cost effectively for the removal of trace organic compounds in natural water namely, mathematical modelling or trial-and error testing. Mathematical modelling is quite complex and requires calibration experimentation while trial-and-error testing can be quite extensive. Equilibrium and kinetic parameters need to be determined to predict the removal of the trace organic compounds from natural water.

Adsorption isotherms describe the thermodynamics of adsorption and are often used to estimate carbon dosages for achieving the required adsorbate removal. Insufficient contact times may result in non-equilibrium conditions, which may limit its use in practice. The effective contact time for PAC in water treatment plants ranges from minutes to hours, which may not be sufficient to reach adsorption equilibrium. Long contact times (nine days) have been reported in the literature in order for 2-MIB to reach equilibrium. The effect of water treatment chemicals may have an indirect impact of the adsorption rate of the PAC. When PAC is dosed into the coagulation basin, floc may adhere to the PAC surface and decrease the rate of adsorption. The Freundlich isotherm equation, is often used because of its accuracy in describing adsorption isotherm data. A straight-line plot relates the amount of adsorbate in the solution phase to that in the adsorbed phase by the following expression:

$$q_e = kC^{1/n} \quad \text{equation 1}$$

where q_e = amount of adsorbate adsorbed per unit weight carbon
 C = equilibrium concentration of adsorbate in solution after adsorption
 k and n are constants.

By taking the logarithm on both sides we obtain:

$$\log q_e = \log k + \frac{1}{n} \log C \quad \text{equation 2}$$

This is an equation of a straight line with a slope of $1/n$ and an intercept of $\log k$. The adsorption isotherms for 2-MIB and geosmin were found to be non-linear over a wide range of equilibrium concentrations.

The pseudo-single-solute homogeneous surface diffusion model (HSDM) has been used to describe the rate of trace organic compound adsorption from natural waters. The HSDM model was originally developed for fixed-bed adsorbers but later applied to PAC as well. The mathematical equations describing the adsorption of a single solute onto PAC for the HSDM are summarised in **Table 7**.

Table 7: Mathematical equations for the HSDM to describe adsorption.

Mathematical equation	Description	Equation no.
$\frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right)$	Rate of change of surface concentration of adsorbate with time at any point within carbon particle.	3
$q(r,0) = 0$	No adsorbate is associated with carbon particle initially.	4
$\frac{\partial q}{\partial r}(0, t = 0)$	Boundary condition required by symmetry of particle.	5
$q(R, t) = \frac{R^2 k_f (C - C_s)}{\rho_c} = \frac{\partial}{\partial r} \int_0^R q r^2 dr$	Equates rate of liquid film diffusion to accumulation rate of adsorbate inside carbon particle.	6
$q(R, t) = q_s = KC_s^{1/n}$	Freundlich isotherm	7
$\frac{dC}{dt} = -\frac{3C_c}{R^3} \frac{\partial}{\partial r} \int_0^R q r^2 dr$	Rate of decrease of adsorbate in the bulk of the solution for a closed-batch reactor.	8
q = adsorbent surface concentration, t = time, r = distance from centre of carbon particle, D_s = surface diffusion coefficient, C = adsorbate concentration in the bulk solution, C_s = adsorbate concentration at the surface of the activated carbon, ρ_c = apparent density of the activated carbon, k_f = surface film diffusion coefficient, q_s = adsorbate concentration at the outer surface of carbon particle.		

The aqueous adsorbate concentration can be determined as a function of time by solving equations 3 and 8 simultaneously with the known boundary and initial conditions. The adsorption rate in water treatment may depend on the film transport or pore diffusion or both. Pore diffusion should control the rate when sufficient agitation is provided. The one assumption that must be met is that pore diffusion is rate limiting. A set of valid Freundlich isotherm constants (equation 7) is required in the HSDM model. The adsorption isotherm can be non-linear in multi-component systems and also be a function of initial adsorbate concentration. Ideal adsorbed solution theory (IAST) has been successfully applied by Crittenden *et al.* to account for the competitive adsorption effect of background organic matter (BOM). BOM is represented by fictive components in IAST. Najm *et. al.* proposed the Equivalent Background Compound (EBC) model, which treats competing BOM as one hypothetical compound. The HSDM has been used with IAST to overcome the problems like

non-linearity as a result of competitive adsorption and the effect of initial adsorbate concentration. The use of IAST with HSDM to simulate kinetic data entails the following:

- a) Conduct single solute isotherm experiment and determine set of Freundlich constants.
- b) Conduct isotherm experiment in natural water with known solute initial concentration.
Fit set of Freundlich constants for each fictive component i using IAST.
- c) Using IAST, generate synthetic isotherm at a different initial solute concentration.
- d) Fit new Freundlich constants with data in c).
- e) Fit D_s for use in HSDM from Freundlich constants in d) along with experimental kinetic data.
- f) Predict solute adsorption kinetics at any initial solute concentration by repeating steps c) and d) to obtain Freundlich constants. Use values along with D_s in step e) in the HSDM.

The proposed solution procedure for the EBC method differs somewhat from the above procedure, although the approach is conceptually similar. The IAST and EBC both assume that the concentration or adsorption characteristics of the background components are constant. The use of IAST or EBC along with the HSDM is clearly not a simple procedure and requires specially trained personnel and time.

The development of a simpler method to predict the capacity of PAC for micropollutants has received attention recently. Knappe *et. al.* showed that, in the presence of competing BOM, the removal percentage of atrazine and 2-MIB was independent of initial micropollutant concentration at any given PAC dosage, provided the micropollutants under discussion were present at trace levels. Atrazine is an example of a more strongly adsorbing compound and 2-MIB of a weaker adsorbing compound. The proportionality between PAC capacity and initial micropollutant concentration was observed for different activated carbons and natural waters. It is therefore concluded by Knappe *et. al.* that the initial concentration dependency of PAC capacity for a micropollutant in natural water can be determined without the use of mathematical models once isotherm data have been collected at a single trace initial concentration in natural water. The upper initial micropollutant concentration limit was not determined and two isotherm experiments were recommended, at the largest anticipated initial micropollutant concentration and a lower initial micropollutant concentration. Gillogly *et. al.* showed that the percent 2-MIB removed by one activated carbon dosage was constant over an initial 2-MIB concentration range of 45 ng/l to 178 µg/l. A single bottle-point isotherm is

recommended to determine the minimum amount of activated carbon necessary to effectively mitigate any 2-MIB taste and odour episode.

CHAPTER 3

METHODOLOGY

3.1 Determination of physico-chemical properties of PAC

The physico-chemical properties of the ten PAC samples used in the evaluation were characterised as follows:

- Moisture content
- Ash content
- Bulk density
- Particle size analysis
- Nitrogen intrusion determination
- Mercury intrusion determination
- Tannin number determination
- Iodine number determination
- Methylene blue number determination
- Geosmin adsorption determination
- 2-MIB adsorption determination

Moisture content: ASTM test method D2867-83 was used.

Ash content: The ash content gives a general indication of the amount of mineral constituents of a carbon. ASTM test method D2866-83 was used.

Bulk density: Samples were analysed by Protechnik laboratories for bulk density.

Particle size analysis: These analyses were performed on the Mastersizer manufactured by Malvern Instrumentation Ltd. A paste was prepared by mixing the PAC sample with liquid dishwashing soap that acted as a wetting and dispersing agent. This paste was added to deionised water until the required obscuration was achieved.

Nitrogen intrusion determination: This technique is used to define the micro- and mesoporosity of porous material but does not provide adequate information on the macroporosity of a sample. Samples were analysed by Protechnik laboratories and standard nitrogen adsorption/ surface area calculations were applied to determine the micropore

volume and surface area (Dubinin-Radushkevich equation). The Brunauer, Emmet and Teller (BET) method was also used to determine surface area and average pore diameter.

Mercury intrusion determination: This technique is used to define the macroporosity of porous material. Samples were analysed by the Physical Chemistry Department at the Potchefstroom University for Christian Higher Education and standard mercury adsorption calculations were applied to determine the total intrusion volume, total pore area and average pore diameter.

Tannin number: The method used is based on the AWWA B600-78 test method and is defined as the concentration of activated carbon (mg/l) required to reduce the standard tannic acid concentration from 20 mg/l to 2 mg/l.

Iodine number: Iodine is a small molecule and iodine number is therefore normally used to describe the tendency of porous material to adsorb smaller molecules. ASTM test method D4607 was used and is defined as the amount of iodine adsorbed (milligrams) adsorbed by one gram of activated carbon.

Methylene blue number: Methylene blue is an aromatic dye and methylene blue number is commonly used to describe the tendency of porous material to adsorb larger molecules. This test determines the reduction in colour and is expressed in milligrams methylene blue removed per gram material.

Geosmin adsorption determination: The results of these tests are referred to as adsorption isotherms in this document. These jar tests are designed to simulate the treatment process and do not allow for enough contact time to reach equilibrium conditions. It was regarded as more important to be able to predict the geosmin adsorptive capacity of the different PAC samples under plant conditions than to predict the equilibrium conditions. The geosmin adsorptive capacity is also influenced by chemicals used in the treatment process and activated sodium silicate and slaked lime will be considered as the standard process. This process is however only used at Rand Water and reference will be made to the processes used at the Cape Metropolitan Council and Umgeni Water. The jar test used to assess the geosmin and 2-MIB adsorption capacities of the different PAC samples is outlined below:

3.2 Equipment

Jar stirrer: Multiple-paddle stirrer equipped with multiple stirring speed settings. The stirring speed to be adjustable between 0 and 300 revolutions per minute (rpm) at each setting.

Blades: Dimensions: 64 mm x 25 mm

Beakers: 1 l square beaker (180 mm x 95 mm x 95 mm approximately)

Syringes: 10 ml & 50 ml

Stop watch

3.3 Test Protocol

3.3.1 Rand Water Procedure

- Six 1-l square jar test beakers were used and filled with 1,2 l of raw water.
- The raw water was dosed with PAC at the required dosage from a stock solution containing a 100 mg/l PAC. The water was mixed for a period of 30 seconds prior to the addition of any chemicals at 300 revolutions per minute (rpm).
- Allowing for addition of two chemicals in the treatment process, chemical A was added at the required dosage followed by chemical B 15 seconds later. The samples were then mixed for a further 30 seconds at 300 rpm. Activated sodium silicate and slaked lime were used as **A** and **B** respectively as coagulants in the standard treatment process at Rand Water.
- The mixing speed was then changed to 200 rpm and mixed for a further 30 seconds.
- The mixing speed was then reduced from 200 to 60 rpm over a period of 30 seconds and mixed for a further 420 seconds (7 minutes).
- The mixing speed was then reduced to 30 rpm for a further 90 seconds after which the stirrer was switched off to allow for a settling period of 15 minutes.
- The supernatant was filtered through Whatman GF/C filters and submitted for geosmin analyses. The GF/C filters were baked at 525°C for 4 hours prior to use. Schott-bottles were used to capture the filtered water for analyses. The bottles were filled to the rim and the opening covered in tin foil before the cap was screwed back onto the bottle.

- The data obtained was fitted to the Freundlich isotherm as described in paragraph 3.1. The amount of PAC required to remove any chosen quantity of geosmin could then be calculated from the Freundlich isotherm equation.

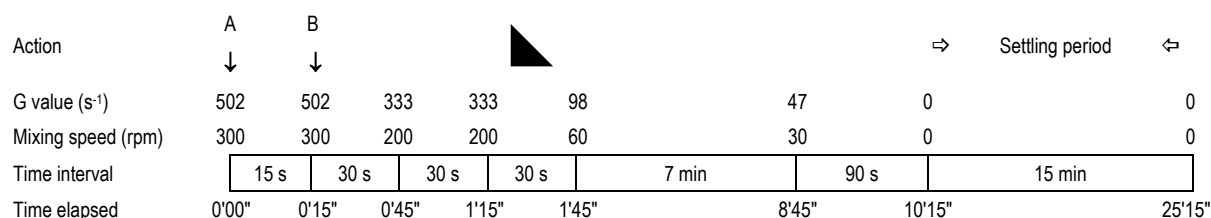


Figure 1: Schematic outline of the high-energy jar test used at Rand Water.

▲ → Direction of gradual energy dissipation.

2-MIB adsorption determinations: The same procedure as for the geosmin adsorption tests was followed.

3.3.2 Umgeni Water Procedure

The geosmin adsorption potential was determined using a modified jar test procedure. A slurry of the PAC was prepared (0,08%) and the required volume of this was then added to 800 ml raw water from the Wiggins Water Works in Durban (Inanda Dam water) which had been spiked to contain 250 ng/l geosmin. Carbon concentrations of 3, 6, 9, 12 and 15 mg/l were used and a control containing no carbon was also prepared. Chemical addition to the water was kept as close as possible to that being used on the plant at the time of sample collection. The same coagulant and dose as being used at the plant was added to each jar and chlorine, lime and bentonite were added if these were being added on the plant at the same concentrations as being used on the plant. The carbon was added to the water while mixing at 40 rpm and a contact time of 20 minutes was allowed. Thereafter the mixing speed was increased to 300 rpm and lime, if required, was added. 30 seconds after the addition of the lime, chlorine was added and after another 30 seconds the coagulant was added. Stirring at 300 rpm continued for 2 minutes after the addition of the coagulant. Thereafter the mixing speed was reduced to 40 rpm and stirring continued for 2 hours. The water was then filtered through Rundfilter M&N filter paper (Whatman No. 1 equivalent) and analysed for geosmin.

3.3.3 Cape Metro Procedure

This method also involves a modified jar test procedure. 600 ml of water was stirred at 700 rpm while 3,6 mg/l Fe (as ferric sulphate) was added together with sufficient saturated

lime solution to maintain the pH at 5,0 and 20 mg/l of PAC. After 30 seconds the stirring speed was dropped to 30 rpm and stirring continued at this speed for another 30 minutes. At the end of the 30-minute slow stir period, the samples were left to settle for another 30 minutes after which 500 ml aliquots were siphoned out of the jars and analysed for geosmin.

3.3.4 Cape Metro Procedure for 850 nm Absorption Test

This procedure involves measurement of the floc formed during the modified jar test procedure described in paragraph 3.3.3 above. A correlation between the absorption of the floc at 850 nm and its geosmin adsorption potential has been observed. The test was carried out exactly as that described in paragraph 3.3.3, except that instead of using raw source waters, distilled water was used and the pH adjusted to between 9,5 and 10 using saturated lime solution. This allowed for better repeatability.

3.4 Effect of Water Quality on the Adsorption of Geosmin

The geosmin adsorption capacity of a particular PAC was determined using different source waters. The adsorption capacity was determined in the following source waters: deionized water, Vaal Dam, Panfontein supernatant, Klip River and spent filter washwater. Vaal Dam water is the raw water supply to treatment plants at Rand Water and is characterized by a high turbidity and fairly high alkalinity. It does not contain many pollutants and has a fairly low total dissolved solids (TDS) concentration. Panfontein supernatant is the water recovered from the high rate gravity thickeners at Rand Water's sludge thickening and disposal site. The pH of the water treatment sludge is adjusted with slaked lime to 11.4 before being pumped to Panfontein. Polyacrylamide flocculant is dosed (0.4 kg/ton sludge) at the inlet to the high rate gravity thickener and the recovered water is blended with Vaal Dam water before being treated at the main purification works at Zuikerbosch. Panfontein supernatant is therefore very high in pH, conductivity, alkalinity and total hardness. Klip River water consists mainly of flow from the wastewater treatment works as well as untreated stormwater runoff from the southern side of Johannesburg. It is characterised by high TDS, total hardness, sulphates and nitrates. Spent filter washwater is similar to Vaal Dam water, except for a much higher suspended solids concentration. The jar test method outlined in paragraph 3.3.1 was used to determine the geosmin adsorption capacity in these waters.

The water used for the Umgeni Water area came from the Wiggins Water Works, which receives its raw water supply from the Inanda Dam. This water is generally low in turbidity, conductivity, hardness, colour and organic matter. The simulated jar tests described in paragraph 3.3.2 were used to assess the various PAC samples on this water.

3.5 Effect of Different Processes on the Adsorption of Geosmin by PAC

The role of water treatment chemicals on the adsorption of taste and odour compounds by activated carbon has received some attention in the literature. It has been shown that water treatment chemicals could impact negatively on the adsorption capacity for taste and odour compounds onto PAC. It was therefore felt necessary to test the effect of some water treatment chemicals on the adsorption capacity of two PAC samples, which were called PAC M and PAC A for the purposes of this study. The main coagulants used in the treatment process at Rand Water are activated sodium silicate and slaked lime. Slaked lime and ferric chloride are also used when the Vaal Dam water contains sufficient alkalinity to buffer the acidifying effect of ferric chloride. Slaked lime and polyelectrolytes or only polyelectrolytes are used as standby chemicals and dosed when the first two options are not available. The effect of the different treatment options were determined using the test protocol described in paragraph 3.3.1. The sequence of addition of the different coagulants for the different treatment options was as follows:

- 60 mg/l slaked lime (A) and 8 mg/l Zetafloc LP526 (B)
- 8 mg/l Zetafloc LP526 (B)
- 2.5 mg/l activated sodium silicate (A) and 60 mg/l slaked lime (B)

The slaked lime dosages are expressed as CaO. Zetafloc LP526 is a cationic polyelectrolyte blend consisting of a polyamine and a polyDADMAC in a 1:1 ratio.

The theory existed that the different water types in the different regions in South Africa would require different types of PAC to effectively remove taste and odour compounds. Five of the ten PAC samples were therefore tested at the Cape Metropolitan Council and Umgeni Water using their own in-house methods. A comparison of the results would indicate if the same PAC could be effective at the three water authorities. If successful, one PAC would potentially be effective at any water treatment plant in South Africa with any combination of coagulants. Water authorities could then enter into discussions with the objective of setting up a centralised stock that could serve all water authorities in South Africa.

The jar test procedure used at the Cape Metropolitan Council to determine the adsorption capacity of PAC is outlined in **Table 8**. In the procedure followed at the Cape Metropolitan Council, geosmin is added to the raw water to a concentration of approximately 200 ng/l. The total volume of water used in the test is usually 600 ml.

Table 8: Jar test procedure used at the Cape Metropolitan Council to assess the removal of geosmin by PAC.

Time (minutes)	Mixing speed (rpm)	
0'00"	700	Addition of 3,6 mg/l Fe as $\text{Fe}_2(\text{SO}_4)_3$.
0'00"	700	Add saturated lime to a pH of 5,0
0'00"	700	Add 20 mg/l of PAC
0'30"	30	Allow flocculation to take place
30'30"	0	Settling period begins
60'30"	0	500 ml aliquots are siphoned off and used for geosmin analysis

The jar test procedure used at the Umgeni Water to determine the adsorption capacity of PAC is outlined in **Table 9**. A slurry of the PAC to be tested is prepared (0.08%, m/v) and the required volume is added to 800 ml raw water from Wiggins Water Works, which had been spiked to contain 250 ng/l geosmin.

Table 9: Jar test procedure used at Umgeni Water to assess the removal of geosmin by PAC.

Time (minutes)	Mixing speed (rpm)	
0'00"	40	PAC added to water at the required dosage
20'00"	300	Lime added at the required dosage.
20'30"	300	Chlorine added at the required dosage.
21'00"	300	Coagulant added at the required dosage
23'00"	40	Flocculation period.
143'00"	0	Filter through Rundfilter M&N filter paper (Whatman no. 1 equivalent) and analyse for geosmin.

The water treated at the Cape Metropolitan Council is regarded as a soft water, low in turbidity and alkalinity and high in colour. Vaal Dam water is regarded as moderately hard,

high in turbidity, moderately high in alkalinity and low in colour. Surface water treated at Umgeni Water is regarded as fairly soft, low in turbidity and alkalinity and low in colour.

3.6 Investigation Into Alternative Methods to select PAC for Geosmin Removal

The effect of initial geosmin concentration on the adsorption capacity for five carbons was also determined. It has been established by Knappe *et al.* that, in the presence of competing BOM, the removal percentage of atrazine and 2-MIB was independent of initial micropollutant concentration at any given PAC dosage, provided the micropollutants under discussion were present at trace levels. The initial concentration dependency of PAC capacity for geosmin in natural water needed to be determined using the jar test methodology to establish if the same conclusion could be reached as that of Knappe *et al.* using static bottle-point isotherm tests. The results would not produce an alternative method to select PAC for geosmin removal, but the PAC dosage could then be determined without the use of mathematical models once isotherm data had been collected at a single trace initial concentration in natural water.

Table 10: Initial geosmin concentrations while testing the effect of initial concentration on adsorption capacity.

PAC	High initial geosmin concentration (ng/l)	Low initial geosmin concentration (ng/l)
M	113	62
A	103	71
T	108	58
I	118	65
O	109	63

Current methods entail the performance of an adsorption isotherm test at one or more PAC dosages and analyses to determine the amount of the taste and odour compound removed. The isotherm test is usually adapted to mimic the conditions at the water treatment plant, which does not allow equilibrium to occur. This approach makes it very costly for water authorities during PAC evaluation and procurement exercises. Smaller water authorities have to rely other water authorities with the necessary infrastructure to evaluate PAC or the carbon supplier to select the best carbon. Most often price only is used as a selection tool, which can result in a product with a lower taste and odour compound adsorption capacity being procured. This can have further financial implications for the water authority when the dosage

required for removing the taste and odour compound below the threshold odour level is high. It is quite clear from the previous paragraph that two different approaches are followed by the Cape Metropolitan Council, Rand Water and Umgeni Water in the evaluation of PAC for taste and odour compound removal. The approaches could be summarised as follow:

- The Cape Metropolitan Council uses jar test methodology based on the treatment process to determine the taste and odour compound removal at 20 mg/l PAC. The least expensive product that removes 90% of the taste and odour compound is selected. Secondary factors such as algal toxin removal are also considered during the PAC evaluation and selection process.
- Umgeni Water and Rand Water use jar test methodology based on the respective treatment processes to determine the taste and odour compound removal at various PAC dosages. The Freundlich isotherm model is applied to the experimental data and the PAC dosage is calculated that will produce the required level of taste and odour compound removal. The dosing cost for each product is calculated and the product with the lowest dosage cost is selected.

The advantages and disadvantages of the first approach to evaluate PAC for taste and odour removal are summarised in **Table 11**.

Table 11: Advantages and disadvantages of the PAC evaluation approach followed by the Cape Metropolitan Council.

Advantages	Disadvantages
• Total evaluation cost is low compared to the second approach. • Evaluation could be performed in relatively short period of time. • Outcome of the approach is the same as the more costly and accurate approach.	• Comparison between products not as empirically correct as in the second approach. • Prediction of dosages to achieve the desired level of removal not possible.

The advantages and disadvantages of the second approach for the evaluation of taste and odour compounds are summarised in **Table 12**.

Table 12: Advantages and disadvantages of the PAC evaluation approach followed by Umgeni Water and Rand Water.

Advantages	Disadvantages
• Method more empirically correct than first approach. • Prediction of dosages to achieve the desired level of removal possible. Experience at Umgeni Water has shown that jar test could be used to predict dosages to be used on full-scale plants.	• Total evaluation cost is very high (4-5 x higher). • Long evaluation period required. • Outcome of the approach is the same as the simpler approach.

Both expertise and the necessary funds to evaluate PAC for taste and odour compound removal are normally lacking in smaller municipalities operating water treatment works. Taste and odour compounds occur at extremely low concentrations and the quantification thereof necessitates specialised techniques and instrumentation. An evaluation of PAC for taste and odour compound removal following either approach is quite costly and usually not within the capacity of smaller municipalities. It was therefore felt necessary to investigate the following:

- correlation between physico-chemical properties of PAC and geosmin removal to establish a specification for PAC suitable for geosmin removal. An alternative method to evaluate PAC could also be established.
- Do a literature survey on new methods available for the analysis of geosmin.
- Investigation into adsorption of compounds that are simple and inexpensive to analyse for and that would also correlate with geosmin removal.
- further explore observations made by personnel at the Cape Metropolitan Council that promise to deliver an simple and inexpensive method to screen PAC samples.

4-Nitrophenol was chosen as an alternative compound to analyse for and to correlate its removal to that of geosmin. A spectrophotometer able to read the absorbance or transmission at 400 nm would be required for the test procedure. In addition, jar stirring equipment would be required to perform the adsorption tests. The test procedure could also be performed in a relatively short period of time. Most water authorities have access to the required equipment, which qualify 4-nitrophenol as a compound that is inexpensive and easy to analyse for. The adsorption test procedure followed to determine the relationship between 4-nitrophenol removal and geosmin removal is outlined in **Table 13**.

Table 13: Outline of the adsorption test for 4-nitrophenol.

Time (minutes)	Mixing speed (rpm)	
0'00"	200	PAC at the required dosage is added to 500 ml of test solution spiked to a 4-nitrophenol concentration of 1 mg/l.
60'00"	0	The solution was filtered through Whatman GF/C filters. The GF/C filters were baked at 525°C for 4 hours prior to use.
		The absorbance of the filtered solution was determined at 400 nm and the concentration read from the calibration graph.
		The data was fitted to the Freundlich isotherm adsorption model and the adsorption capacity expressed as X/M_{80} (mg 4-nitrophenol removed/mg carbon)

A correlation between the floc colour obtained in the jar test and the geosmin removal capacity was noticed by staff members at the Cape Metropolitan Council. Enquiries into analytical techniques available to measure the floc colour intensity by contacting specialists in the paint industry was not of any assistance. An instrument used to measure the stability of emulsions was made available to the Cape Metropolitan Council for a trial period. The instrument is marketed under the trade name "Turbiscan" by Micron Scientific in South Africa and measures the absorbance at 850 nm by scanning along the length of the measuring tube. Some correlations were noticed between the adsorbance at 850 nm and the geosmin removal for the activated carbon. This has led to a simplified procedure on standard spectrophotometric equipment available in most laboratories by which the absorbance was determined at 850 nm. The exercise was repeated on a limited number of samples at Umgeni Water and Rand Water and some correlations were observed. Data from the Cape Metropolitan Council was further explored to determine the suitability of this method.

Zeta potential measurements: The determinations were performed on a Zetamaster manufactured by Malvern Instrumentation. Samples were prepared in tap water to achieve a high enough TDS concentration for adequate conductance to make the measurements.

X-Ray Photoelectron Spectroscopy (XPS): XPS is a powerful technique to study the surfaces of materials and were used by other researchers [,] to determine the surface chemistry of carbon fibres. XPS-analyses were performed by the University of Pretoria on PAC A and PAC F to determine the differences in surface oxide concentrations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Determination of physico-chemical properties of PAC

The results from the moisture, ash content and bulk density are summarised in **Table 14**. The moisture content of the material should be within the manufacturer's specification at the time of packaging, but could exceed the maximum specification by the time it is delivered at the water treatment plant. The ash content of activated carbon has no real significance for the customer if the material has a high adsorbing capacity for taste and odour compounds. Ash content might be of value for quality control purposes to the customer. The bulk density of the material is important to the customer to determine the storage space required to keep enough stock to ensure effective treatment of the raw water during periods of taste and odour incidents.

The PAC samples are arranged in descending order of geosmin adsorbing capacity expressed as amount of geosmin removed per gram of carbon. No specific type of raw material used in the manufacture of the different PAC brands and/ or grades produce PAC that shows better taste and odour adsorbing capacity.

The statistical calculations describing the particle size of the different PAC samples are summarised in **Table 15**. Particle size influences the adsorption kinetics and choosing a product with a smaller particle size might benefit water treatment plants with very short retention times.

Particle size distribution could be important for recharging silos with hopper systems. Practical experience has shown that material with a large particle size distribution tends to compact and reduce the amount of material that can be fed through a hopper. Material with a small particle size distribution can be fed through a hopper at a much faster rate.

Table 14: Summary of the physical properties of ten PAC samples.

PAC			Moisture (%)	Ash (%)	Bulk density (g.cm ⁻³)
M	Analytical result	Wood	1.84	7.09	0.24
	<i>Specifications</i>		<i>max 6</i>	<i>Max 8</i>	<i>0.2-0.35</i>
A	Analytical result	Peat	2.19	7.75	0.21
	<i>Specifications</i>		<i>max 5</i>	<i>Max 10</i>	<i>0.2</i>
T	Analytical result	Coal	2.09	13.29	0.32
	<i>Specifications</i>		<i>4 - 8</i>		<i>0.3-0.4</i>
I	Analytical result	Wood	8.01	3.42	0.37
	<i>Specifications</i>		<i>max 5</i>	<i>Max 6</i>	<i>0.3-0.4</i>
U	Analytical result	Not specified	5.28	5.05	
	<i>Specifications</i>		<i>max 10</i>	<i>Max 6</i>	<i>0.55</i>
D	Analytical result	Wood	8.71	6.06	0.39
	<i>Specifications</i>		<i>max 12</i>		<i>0.43</i>
O	Analytical result	Wood	4.13	6.79	0.35
	<i>Specifications</i>		<i>6 - 8</i>	<i>4 - 8</i>	<i>0.4-0.45</i>
F	Analytical result	Wood	0.67	4.94	0.29
	<i>Specifications</i>		<i>max 8</i>		<i>0.25-0.6</i>
R	Analytical result	Bituminous coal	2.98	14.92	0.36
	<i>Specifications</i>		<i>max 8</i>		<i>0.5</i>
P	Analytical result	Coal	0.67	14.67	0.35
	<i>Specifications</i>		<i>max 8</i>		<i>0.5</i>

Table 15: Particle size analyses results for ten PAC samples.

PAC	Particle Size Result Statistics (µm)				
	D(v,0.1)	D(v,0.5)	D(v,0.9)	D[4,3]	D[3,2]
M	6.69	23.26	111.35	42.84	15.56
A	4.32	14.85	86.86	33.63	9.88
T	5.57	22.81	69.87	31.36	13.12
I	4.91	23.61	108.34	52.61	12.26
U	5.28	16.15	85.59	32.83	11.55
D	5.06	20.34	82.41	33.83	11.81
O	9.59	33.01	98.19	45.19	21.31
F	8.72	27.94	73.04	36.94	18.80
R	4.70	20.12	63.09	27.77	11.14
P	6.76	29.50	77.50	36.55	16.02

A comparison of the degree of microporosity of the different carbons is described through the parameters listed in **Table 16**.

Table 16: Description of the porosity of the different PAC samples as determined from the nitrogen intrusion studies.

PAC	T plot		BJH	BET	
	Micropore volume (m ³ /g)	Micropore area (m ² /g)	Pore volume (m ³ /g)	Surface area (m ² /g)	Average pore diameter (Å)
M	0.3506	744.7988	0.4025	982.5875	26.9013
A	0.4034	869.2899	0.5016	1092.7823	28.5507
T	0.3892	831.1271	0.4425	1048.1384	26.0547
I	0.3993	859.9136	0.2038	964.9851	22.7698
D	0.4209	905.4252	0.2325	1027.3730	23.0144
O	0.3799	813.5159	0.2681	961.5545	23.7733
F	0.2982	635.7882	0.2983	853.2284	25.8996
R	0.3363	712.7630	0.3436	925.9483	24.3684
P	0.3990	853.5870	0.3720	1055.3936	24.6563

Table 17: Description of the porosity of the different PAC samples as determined from the mercury intrusion studies.

	Total intrusion volume (ml/g)	Total pore area (m ² /g)	Average Pore Diameter by 4V/A (μm)	Porosity (%)
M	1.9753	60.1700	0.1313	70.3111
A	1.9747	22.0790	0.3577	62.9196
T	1.0793	30.4530	0.1418	52.1985
I	1.1740	46.4500	0.1011	59.2338
D	1.1155	44.5180	0.1002	58.1263
O	1.9922	56.7030	0.1405	72.4013
F	1.8344	4.3540	1.6853	65.9957
R	1.2024	53.1410	0.0905	59.3944
P	1.3839	70.1950	0.0789	62.5483

A comparison of the degree of macroporosity of the different carbons is described through the parameters listed in **Table 17**.

The pore surface area and average pore diameter for PAC F differed by a factor of ten compared to the other activated carbons tested. Despite querying the results, no explanation was received which could account for the difference.

The adsorption capacity of the ten PAC's for tannic acid, iodine and methylene blue was determined and the results are displayed in **Table 18**. The PAC samples are arranged in descending order of geosmin adsorption capacity as expressed by the mass of geosmin removed (ng) per mass of carbon (mg).

Table 18: Tannin-, iodine- and methylene blue numbers for ten PAC's tested at Rand Water.

PAC	Tannin value	Iodine Value	Methylene blue number
M	132	973	22.6
A	139	1065	23.1
T	234	950	24.1
I	363	917	21.2
U	304	882	
D	358	823	20.8
O	361	616	20.8
F	296	992	18.6
R	244	981	20.3
P	322	981	23.8

The geosmin adsorption capacity of the different carbons was determined as described in paragraph 3.3.1. Vaal Dam water was spiked to a concentration of approximately 120 ng/l. The initial geosmin concentration used was determined by the detection limit of the analytical determination of geosmin. The analytical detection limit of geosmin at Rand Water is 10 ng/l. PAC with a high geosmin adsorption capacity is able to remove more than 90% of the geosmin present. The graphical illustration of the Freundlich isotherm equations for the different PAC samples in **Table 19** are displayed in **Figure 17** to **Figure 26** in the appendix. The PAC dosages required to achieve 80% removal and X/M_{80} in **Table 19** are calculated from the Freundlich equation for each PAC.

The PAC samples are arranged in descending order of geosmin adsorption capacity (X/M_{80}) in **Table 19**. The PAC dosage to achieve 80% geosmin removal was not used as a measure of adsorption capacity due to the differences in initial geosmin concentration.

Table 19: A comparison of the geosmin adsorption capacity of ten PAC samples.

PAC	C_0 (ng/l)	C_{80} (ng/l)	PAC dosage (mg/l)	% Geosmin removal	X/M_{80} (ng geosmin removed/ mg C)
M	113	22.6	11.6	80	7.8
A	103	20.6	10.7	80	7.7
T	108	21.6	13.7	80	6.3
I	118	23.6	17.0	80	5.6
U	117	23.4	17.5	80	5.4
D	127	25.4	19.2	80	5.3
O	109	21.8	17.1	80	5.1
F	124	24.8	21.5	80	4.6
R	75	15.0	17.9	80	3.4
P	105	21.0	28.1	80	3.0

C_0 = initial geosmin concentration during isotherm determination

C_{80} = geosmin concentration after 80% removal. Calculated from the Freundlich equation.

PAC dosage = calculated from the Freundlich equation to remove 80% geosmin.

X/M_{80} = ng geosmin removed per mg PAC for 80% removal.

The geosmin adsorption capacity of six of the ten PAC's used was also determined in the presence of 2-MIB ($C_0 = \pm 350$ ng/l). The results are graphically displayed in **Figure 2**. It can be concluded from the results that the geosmin adsorption capacity of PAC is not affected by the presence of 2-MIB. The adsorbability of geosmin onto PAC is better than the adsorbability 2-MIB and the 2-MIB adsorption capacity of PAC may well be affected by the presence of geosmin. The presence of geosmin on the removal of 2-MIB has not been investigated since geosmin is the major taste and odour compound found in surface water treated by the Cape Metropolitan Council, Rand Water and Umgeni Water.

The 2-MIB adsorption capacity of five of the ten PAC samples was determined in the presence of geosmin. The graphical representation of the 2-MIB Freundlich isotherms is shown in the appendix (**Figure 28**). The Freundlich model for 2-MIB did not fit the experimental data as well as for the geosmin removal data as shown by a comparison of the R^2 -values (**Figure 17 to Figure 26 versus Figure 27**). The same observations were made at

Umgeni Water, which is ascribed to a lower accuracy for the 2-MIB analyses. The PAC dosage required to achieve 80% 2-MIB removal and mass of 2-MIB removed (ng) per mass carbon (mg) were calculated from the Freundlich isotherms and are summarised in **Table 20**.

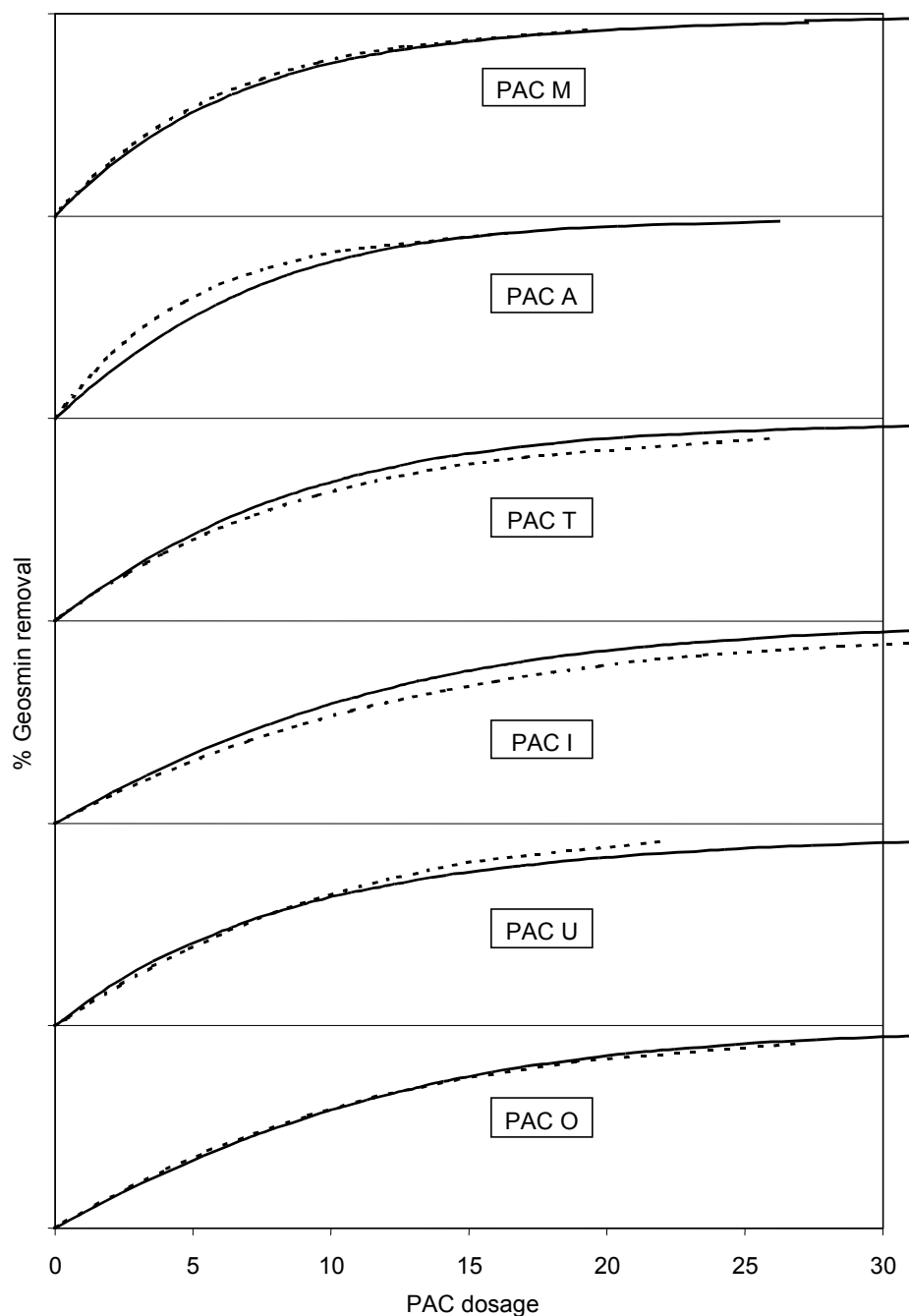


Figure 2: Graphical representation of geosmin removal as a function of PAC dosage. The solid line represents the removal with only geosmin present and the dotted line the removal in the presence of ± 350 ng/l 2-MIB.

Significantly higher dosages are required to achieve 80% 2-MIB removal compared to that of geosmin removal. It would therefore be expected that higher PAC dosages would be required to remove 2-MIB below threshold odour levels compared to that of geosmin.

Table 20: 2-MIB adsorption capacity of five PAC's in the presence of geosmin.

PAC	C_0 (ng/l)	C_{80} (ng/l)	PAC dosage (mg/l)	% 2-MIB removal	X/M ₈₀ (ng 2-MIB removed/ mg C)
M	344	68.8	18.6	80	1.170
T	321	64.2	18.0	80	1.154
A	339	67.8	22.6	80	1.080
O	355	71	32.5	80	0.942
I	355	71	35.1	80	0.908

C_0 = initial 2-MIB concentration during isotherm determination

C_{80} = 2-MIB concentration after 80% removal. Calculated from the Freundlich equation.

PAC dosage = calculated from the Freundlich equation to remove 80% 2-MIB.

X/M₈₀ = ng 2-MIB removed per mg PAC for 80% removal.

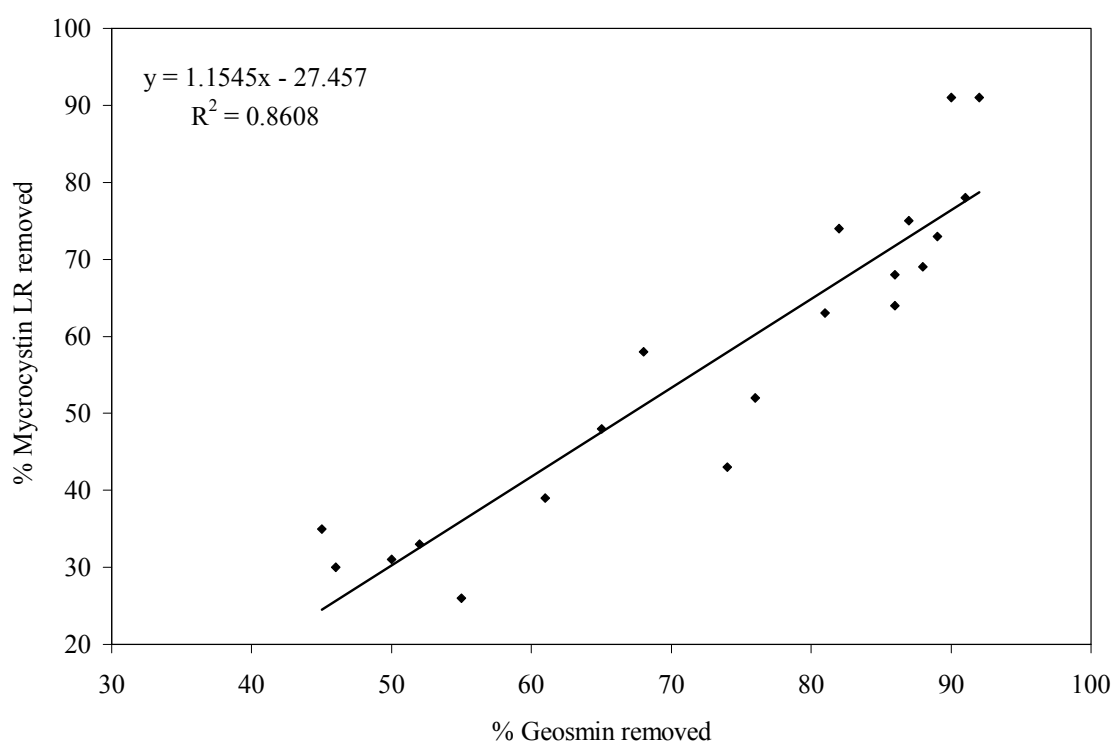


Figure 3: Graphical representation of the relationship between myrocystin-LR and geosmin adsorption capacity.

The relationship between microcystin-LR adsorption capacity and geosmin adsorption capacity is graphically displayed in **Figure 3**. A general linear trend exists that illustrates that carbons that have a high geosmin adsorption capacity should also display a high microcystin-LR adsorption capacity. However, the fit is not good enough to assume that the previous statement would be true for all carbons. Water authorities that need to remove both these compounds from the water, should base their evaluation procedure on the removal of both compounds.

4.2 Effect of Water Quality on the Adsorption of Geosmin

The effect of water quality on the adsorption of geosmin was determined in different water sources that would represent the extremes in terms of some of the water quality parameters important to water treatment. The water quality of the different sources used is summarised in **Table 21** (see also paragraph 3.4).

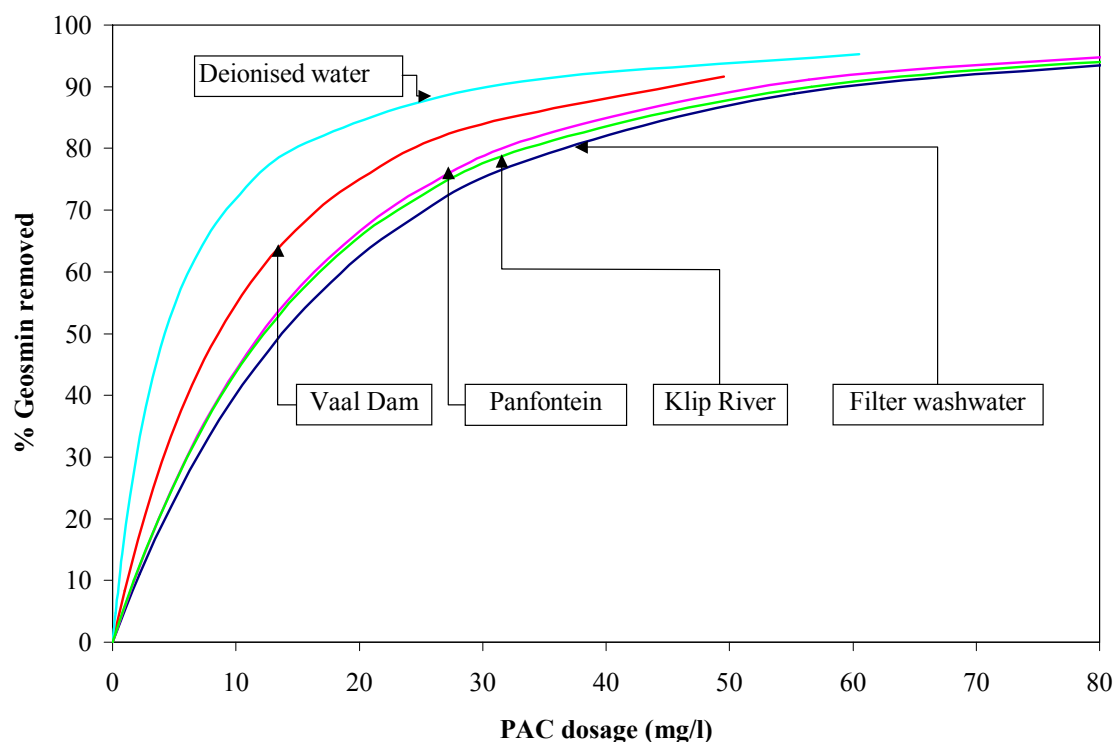


Figure 4: Adsorption isotherm for geosmin in different waters.

Table 21: Water quality of the different water sources used.

Parameter	Deionised water	Vaal Dam	Panfontein supernatant	Klipriver	Spent filter washwater
Conductivity at 25°C (mS/m)	0.11	26	180	74	24
pH		8.2	11.9	8.2	8.5
Colour (mg/l Pt)		20	180	45	29
TDS (mg/l)		160	512	545	140
Alkalinity (mg/l as CaCO ₃)		98	557	94	75
Total hardness (mg/l as CaCO ₃)		91	525	255	76
Calcium (mg/l as Ca)		21	211	60	19
Magnesium (mg/l as Mg)		11	0.1	26	7
Sodium (mg/l as Na)		18	22	48	16
Potassium (mg/l as K)		4	6	11	4
Cadmium (mg/l as Cd)		<0.05	<0.05	<0.05	<0.05
Chromium (mg/l as Cr)		<0.05	<0.05	<0.05	<0.05
Cobalt (mg/l as Co)		<0.10	<0.10	<0.10	<0.10
Copper (mg/l as Cu)		<0.10	<0.10	<0.10	<0.10
Iron (mg/l as Fe)		0.33	<0.05	<0.05	<0.05
Manganese (mg/l as Mn)		<0.10	<0.10	<0.10	<0.10
Lead (mg/l as Pb)		<0.10	<0.10	<0.10	<0.10
Zinc (mg/l as Zn)		<0.10	<0.10	<0.10	<0.10
Nickel (mg/l as Ni)		<0.10	<0.10	<0.10	<0.10
Aluminium (mg/l as Al)		0.43	<0.10	<0.10	<0.10
Boron (mg/l as B)		<0.10	<0.10	<0.10	<0.10
Vanadium (mg/l as V)		<0.10	<0.10	<0.10	<0.10
Molybdenum (mg/l as Mo)		<0.10	<0.10	<0.10	<0.10
Total silica (mg/l as SiO ₂)		1.4	<0.10	0.23	NA
Nitrate (mg/l as N)		<0.10	0.22	2.95	0.24
Ortho phosphate (mg/l as P)		0.23	0.06	0.91	0.05
Total phosphorous (mg/l as P)		2.2	0.75	1.4	0.51
Sulphate (mg/l as SO ₄ ²⁻)		19	18	188	17
Chloride (mg/l as Cl ⁻)		5.1	5.6	4.5	4.5

Geosmin removal as a function of PAC dosage in different types of water is graphically displayed in **Figure 4**. The highest geosmin removal was observed in deionised water followed by Vaal Dam water. The result for deionised water was expected due to the absence interfering substances. Similar geosmin removal was observed for Klip River and Panfontein supernatant. The lowest geosmin removal was observed for the spent filter washwater. Spent

filer washwater contains the highest amount of suspended solids, but is similar to Vaal Dam water in terms of the other water quality parameters. The effect of suspended solids seems to be more pronounced than that of total dissolved solids. A possible explanation of the effect of suspended solids might be that PAC becomes enmeshed in the flocculated material during coagulation, which limits diffusion to the particles and results in lower removals.

4.3 Effect of Different Processes on the Adsorption of Geosmin by PAC

The effect of different water treatment processes on the adsorption capacity of geosmin as assessed by the PAC dosage requirement for different removals are summarised in **Table 22**. The graphical representation of geosmin removal as a function of PAC dosage is illustrated in the appendix (**Figure 29** and **Figure 30**).

The lowest PAC dosages were observed for the slaked lime and polyelectrolyte process. The dosages for the polyelectrolyte process only were slightly higher than that of the combined slaked lime and polyelectrolyte process. It is therefore quite clear that the dosing of slaked lime would not be detrimental to the adsorption process. The highest PAC dosages were required for the activated sodium silicate and slaked lime process. The dosing of activated sodium silicate appears to reduce the adsorption capacity of the PAC and higher PAC dosages are therefore required to result in the same geosmin removal as the other two processes.

Table 22: PAC dosage requirements (mg/l) respectively for 60, 70 and 80% geosmin removal with different treatment processes at Rand Water.

PAC and Process	% Geosmin removal		
	60	70	80
	mg/l PAC dosage		
PAC M (lime, 526)	5.3	7.1	10.1
PAC M (526)	5.6	7.6	10.8
PAC M (lime, silica)	6.8	9.0	12.3
PAC A (lime, 526)	3.9	5.2	7.3
PAC A (526)	4.6	6.3	9.2
PAC A (lime, silica)	6.7	8.6	11.3

The results from the evaluation of five of the ten PAC samples at the different water authorities are summarised in **Table 23**. The geosmin removal at 15 mg/l PAC dosage was calculated from the Freundlich isotherm data for the Rand Water evaluation. That enabled the project team to compare the same adsorption efficiency parameter for the three evaluations and to rate the carbons accordingly. It has already been established in paragraph 4.1 (as tested by Rand Water) that the geosmin removal capacity of PAC M and A are almost the same. Similar results were achieved in the tests at the other two water authorities. PAC I performed better at the Cape Metropolitan Council and Umgeni Water compared to the test at Rand Water. In general, the order of adsorption capacity of the different products at the three water authorities was similar. It could therefore be concluded that a PAC that shows a high geosmin adsorption capacity when tested by one water authority should also display a high geosmin adsorption capacity when tested by another water authority under a different set of conditions. When the adsorption capacity of a PAC is adversely affected by the water quality or the test conditions, all other PAC types should be affected to more or less the same extent.

The result above emphasized that water quality would not unduly influence the type of PAC that would be effective at a particular water authority, but only the dosage required to achieve the desired level of removal. It would therefore be possible to use a centralised stock to serve all water authorities in South Africa. This is also illustrated by the types of PAC that have been used at the different water authorities. PAC A has been used at the Cape Metropolitan Council and Rand Water.

Table 23: Results for geosmin removal using jar test methods based on the treatment processes at the respective water authorities.

PAC	Rand Water		Cape Metropolitan Council		Umgeni Water	
	% geosmin removed at 15 mg/l	Rating	% geosmin removed at 20 mg/l	Rating	% geosmin removed at 15 mg/l	Rating
A	89	1	93	1	96	2
M	85	2	92	2	97	1
T	83	3	79	4	88	4
I	82	4	84	3	93	3
O	79	5	68	5	88	5

4.4 Investigation Into Alternative Methods to select PAC for Geosmin Removal

The results from the investigation (**Figure 5**) of the effect of initial geosmin concentration on the adsorption capacity clearly illustrate the independency thereof on the adsorption capacity. PAC O was the only PAC that did not support this initial observation. The Freundlich isotherm equation for the lower concentration was however generated from two points only and any inaccuracy in the geosmin analysis would have had a marked effect on the comparison. The value of this exercise is that the adsorption test could be performed at any practical initial trace level concentration for the taste and odour compound of interest and PAC dosages could then be extrapolated for any other initial trace level concentration.

An attempt was also made to correlate the physico-chemical properties of the 10 PAC samples detailed in paragraph 3.3.1 to the geosmin adsorption capacity. The surface area available for the adsorption of organic compounds is the result of the internal pore structure of the carbon. If it is assumed that geosmin would be taken up into the micro- and/ or mesopore area of the activated carbon, then a correlation should exist between the pore parameters determined through nitrogen intrusion measurements. However, it is clear from **Figure 6** that no correlation exists between geosmin removal and the micropore volume, surface area (t-plot), or BJH pore volume. Also **Figure 7** shows that BET surface area and average pore diameter did not correlate with the geosmin adsorption capacity of the different PAC samples. The lack of correlation shows that the mechanism of adsorption is not well understood.

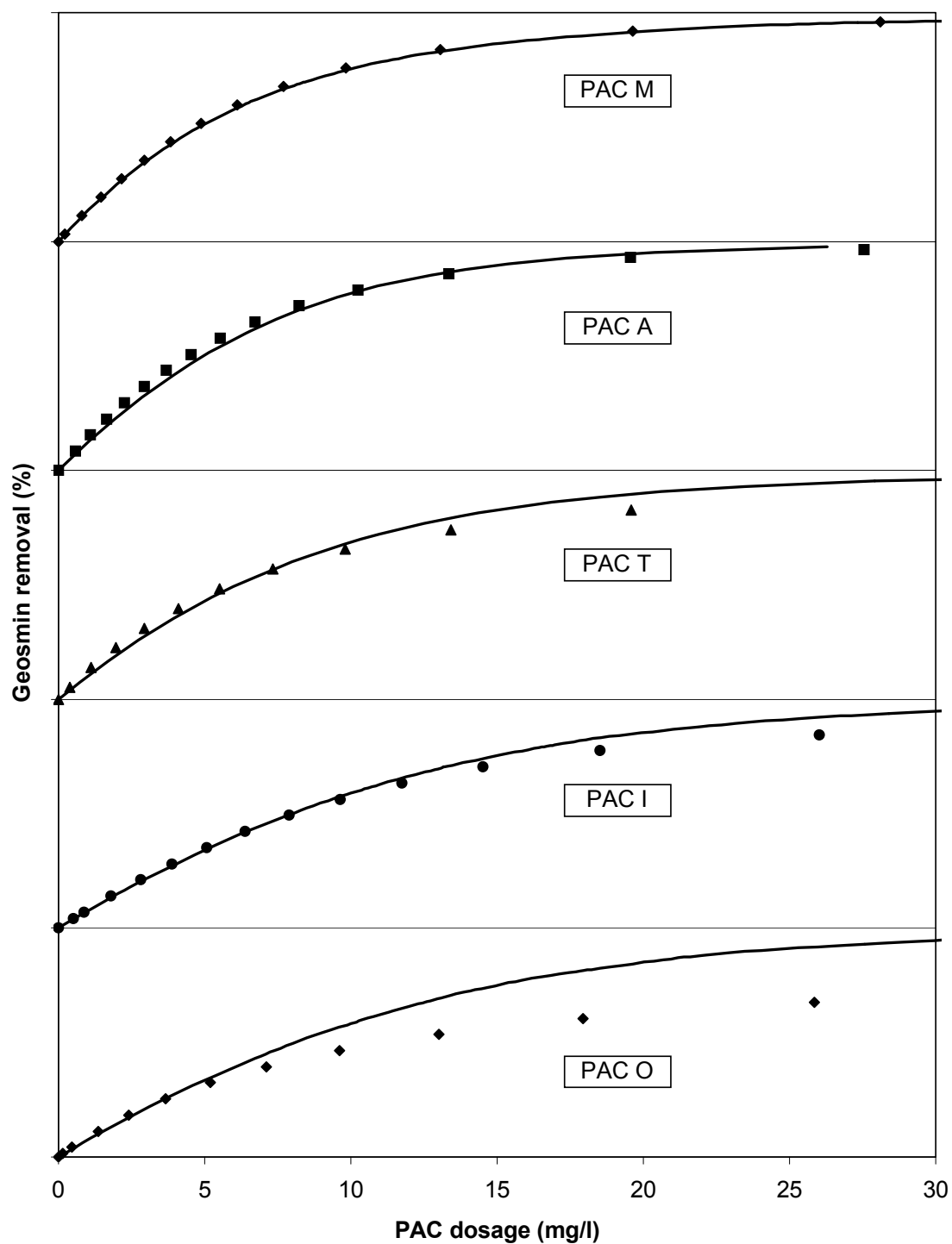


Figure 5: Geosmin adsorption capacity at different initial geosmin concentrations. The solid line and the data points represent the removal at high and low initial concentration respectively.

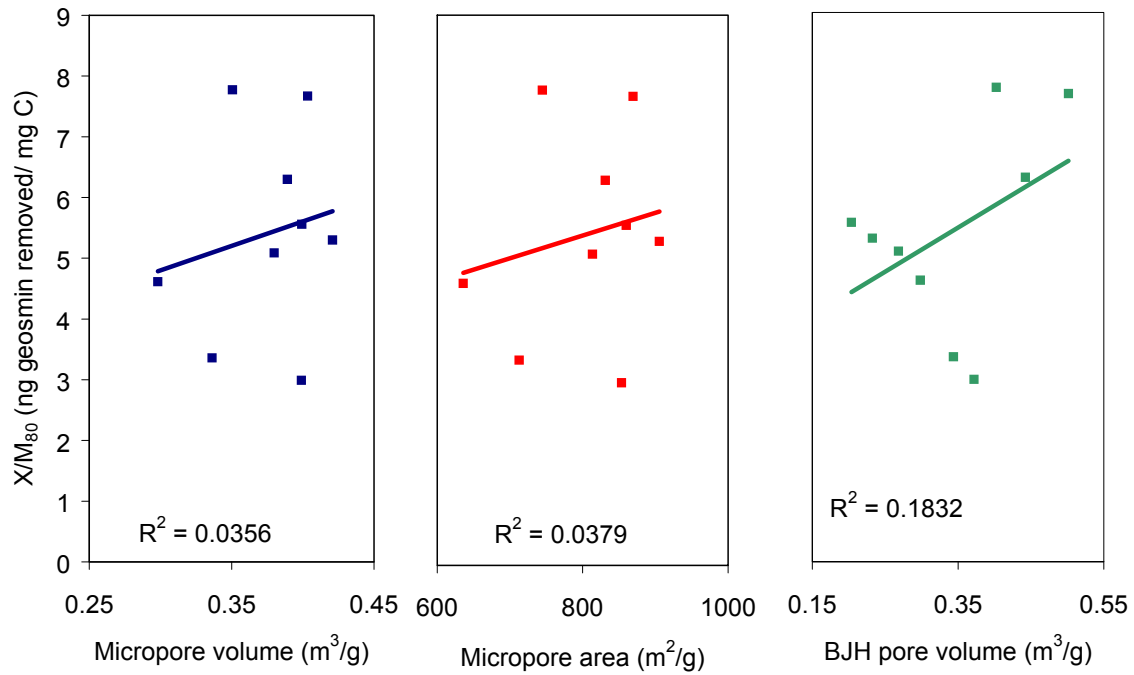


Figure 6: Graphical representation of the correlation between geosmin adsorption capacity, the t-plot micropore volume and area and BJH pore volume.

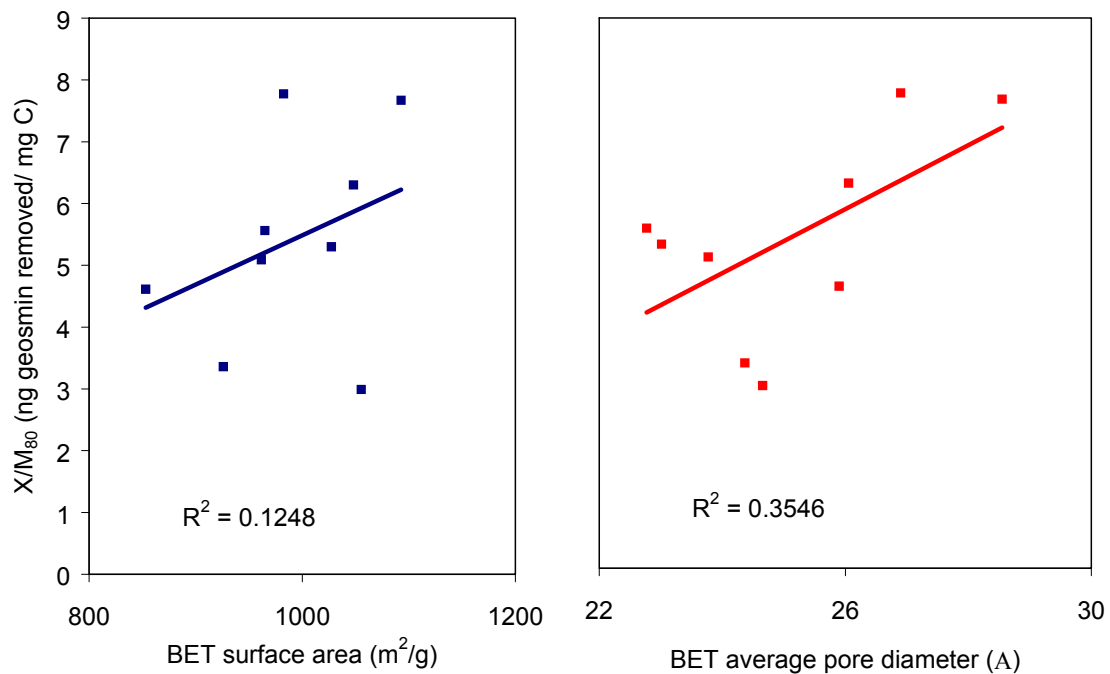


Figure 7: Graphical representation of the correlation between geosmin adsorption capacity, the BET surface area and average pore diameter.

The correlation between PAC porosity as determined through mercury intrusion studies and the geosmin adsorption capacity of the different PAC samples were also investigated and again no correlation could be found as illustrated in **Figure 8**. The average pore diameter of one of the PAC samples was significantly higher (by a factor 10) than the other carbons. Omitting that sample from the series did improve the fit (R^2) to the linear trendline but no correlation between PAC properties and geosmin adsorption was observed.

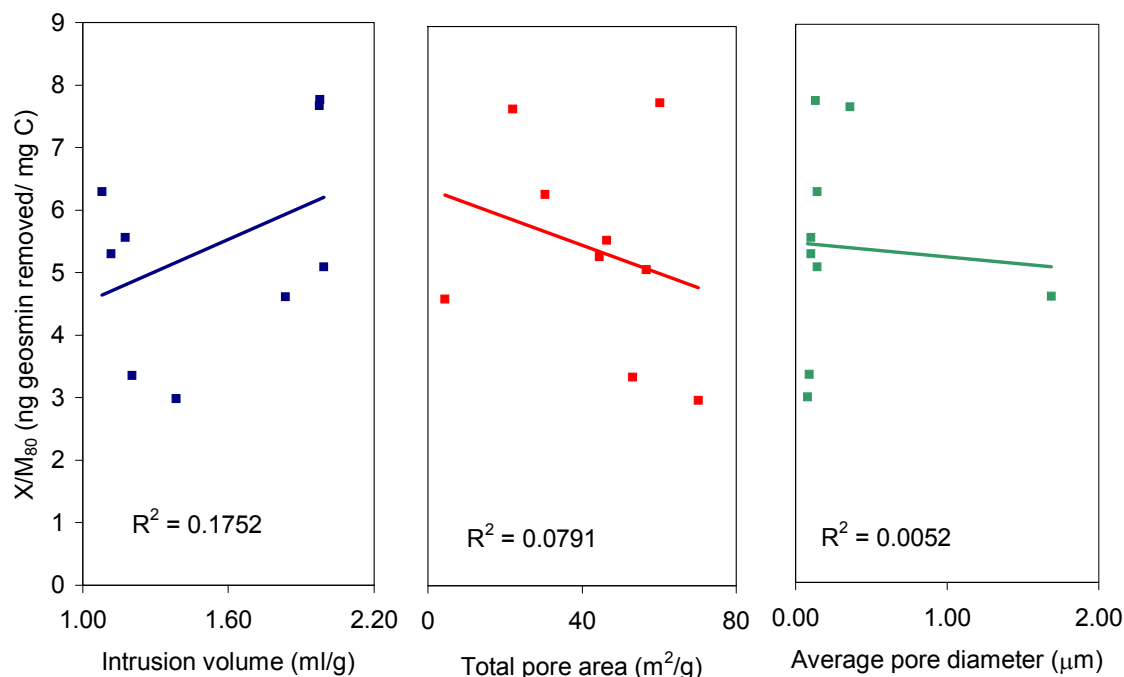


Figure 8: Relationship between the porosity of the different carbons and geosmin adsorption capacity as determined through mercury intrusion studies.

The correlations between tannin-, iodine- and methylene blue numbers and geosmin removal were also investigated for the 10 PAC samples used in this project. An inverse trend between tannin number and geosmin adsorption capacity was observed, although it would not be considered as a good correlation (**Figure 9**). Eleven different PAC samples were also tested for tannin-, iodine- and methylene blue number at Umgeni Water and the results were plotted against geosmin adsorption capacity (**Figure 10**). The same observation was made for these results on the relationship between tannin number and geosmin adsorption capacity. PAC samples with a tannin number of less than 200 showed good geosmin adsorption capacity. The relationships between iodine-, methylene blue number and geosmin adsorption capacity were also investigated by Umgeni Water and again, no correlation was found.

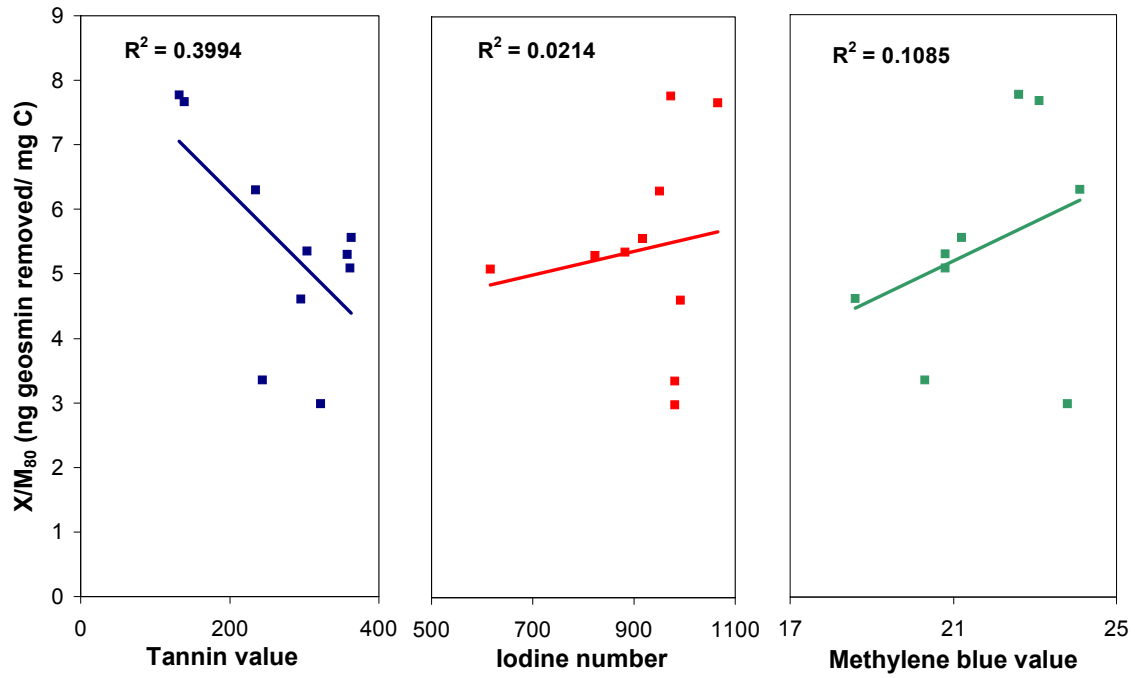


Figure 9: Correlation between geosmin removal and tannin-, iodine- and methylene blue number tested for ten different carbons at Rand Water.

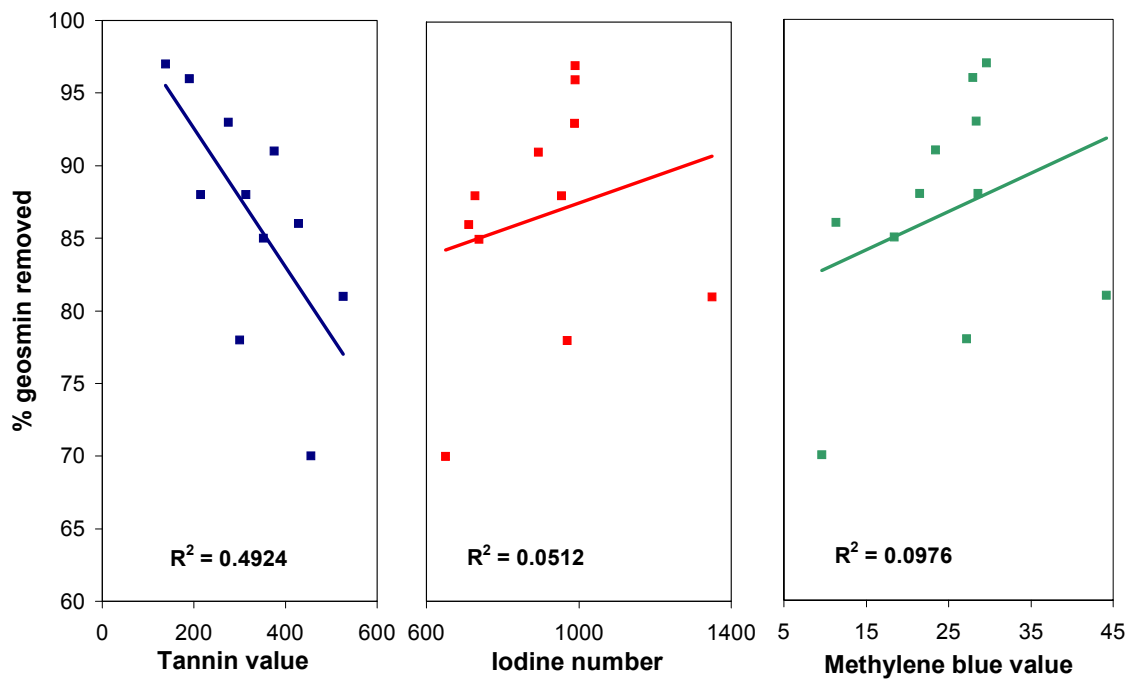


Figure 10: Correlation between geosmin removal and tannin-, iodine- and methylene blue number tested for eleven different carbons at Umgeni Water.

Based on these correlations it would appear that tannin number has limited predictive value for geosmin adsorption, but that iodine and methylene blue numbers are of no use for this purpose whatsoever.

Geosmin analysis is a very expensive analytical method due to the laborious sample preparation and sophisticated analytical instrumentation that is required. The project team thus felt that it might be useful to look into alternate methods for geosmin analysis. **Table 24** gives an overview of the possible alternate methods but none of these methods proved to be viable or more cost effective for the routine analysis of geosmin compared to existing methods.

Table 24: List of references for alternate quantitative analytical methods methods.

Reference	Method	Detection limit
Naphthol-modified β -cyclodextrins as fluorescent sensors for detecting contaminants in drinking water.	Fluorescence @ 505 and 485 nm	Not specified
Use of an electronic nose to detect tainting compounds in raw and treated potable water.	Electronic nose	Not specified
Determination of 2-MIB in odorous water by immunoassay	ELISA	Not specified
Analysis of volatile liquids or solutions	Gas sensor	Not specified

The graphical illustration of the Freundlich isotherm equations for 4-nitrophenol with the different PAC samples is displayed in **Figure 31** to **Figure 40** in the appendix. The correlation between 4-nitrophenol and geosmin adsorption capacity is illustrated in **Figure 11**. Similar observations were made with the correlation between tannin number and geosmin adsorption capacity. An inverse trend exists between 4-nitrophenol adsorption capacity and geosmin adsorption capacity, although it would not be considered as a good correlation.

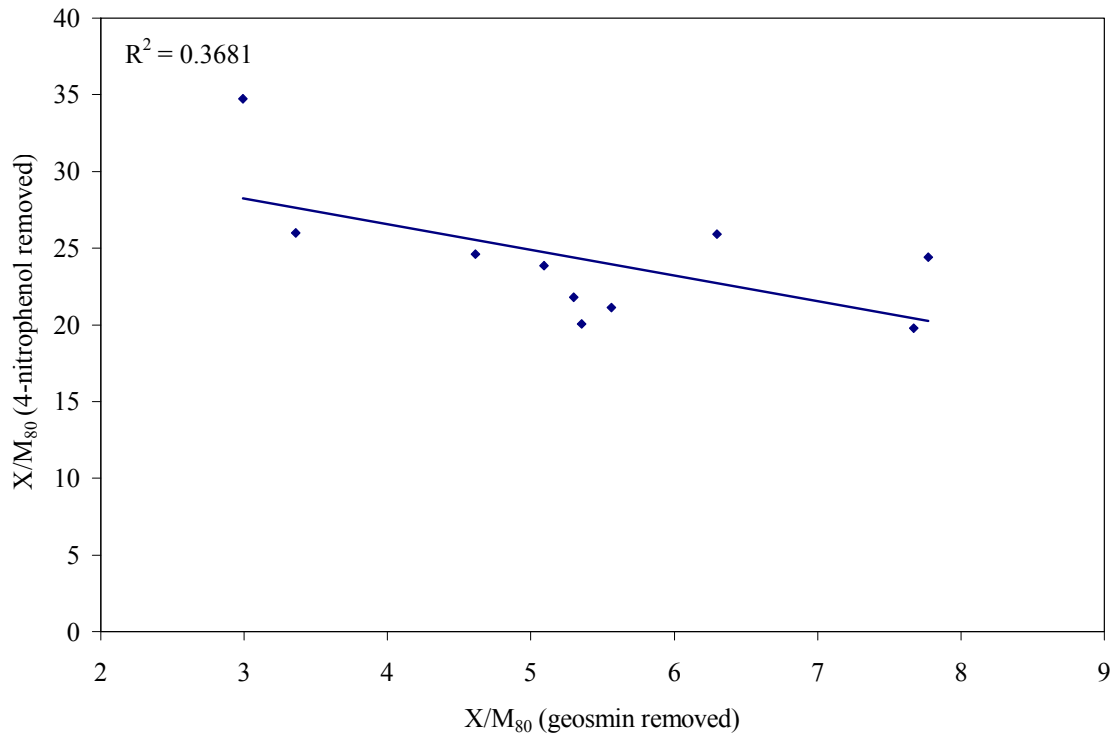


Figure 11: Relationship between 4-nitrophenol and geosmin removal by ten PAC's.

As noted under paragraph 3.6, observations were made at the Cape Metropolitan Council that indicated that a correlation could exist between the colour of the PAC/coagulant floc obtained in the jar test and geosmin adsorption capacity. The test was performed on the 10 different PAC samples used in this project at Rand Water using the activated sodium silicate and slaked lime process and the polyelectrolyte process. The objectives of the exercise were twofold, namely:

- to reproduce the observation made at the Cape Metropolitan Council on a different water and treatment process.
- to test the effect of the different treatment chemicals on the floc colour ratings.

The different PAC samples were rated according to the floc colour or intensity after settling while still in the jar. A predetermined volume of flocculated material was also taken from the jar while it was still being mixed and this was then filtered. After filtration, the filter papers were left to dry before being rated. The filter papers were arranged in order according to the floc colour and intensity and a scanned image was produced and included in this report to illustrate the observation to the reader. The image was not scanned at the highest resolution in order to produce a file that was still manageable. Although some detail was lost in the process, the reader should still be able to recognise the difference in colour intensity between

the different PAC samples (**Figure 12**). The ratings for the different carbons obtained for the two processes are summarised in **Table 25**. The carbon with the darkest floc colour is rated as one.

Table 25: Floc colour rating of the different PAC samples.

PAC	X/M ₈₀ (ng geosmin removed/ mg C)	Activated sodium silicate and slaked lime		Polyelectrolyte	
		Settled	Filtered	Settled	Filtered
M	7.8	2	2	3	3
A	7.7	1	1	1	1
T	6.3	5	6	6	7
I	5.6	7	9	7	4
U	5.4	3	3	2	2
D	5.3	4	4	5	5
O	5.1	9	10	10	10
F	4.6	8	8	8	8
R	3.4	6	5	4	6
P	3.0	10	7	9	9

The following observations were made based on the results of the “floc colour” test:

- The differences in floc colour were extremely difficult to judge in some cases and the rating was found to be subjective.
- The differences in floc colour were more difficult to judge for the polyelectrolyte process.
- Although the ratings often correlated with the geosmin adsorption capacity, this was not always the case.

The “floc colour” test would therefore not be recommended for the purpose of selecting or screening PAC samples for the removal of geosmin.

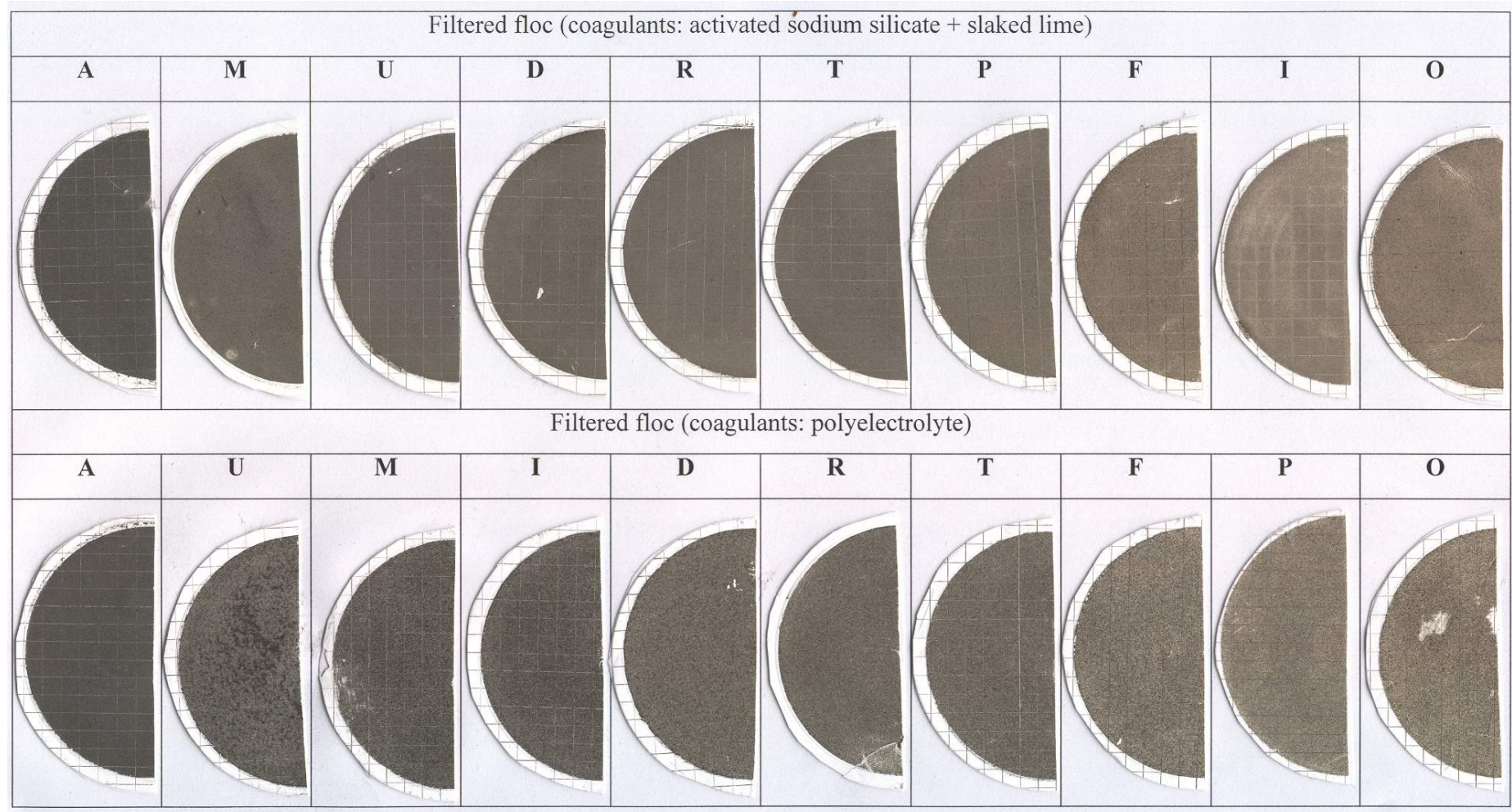


Figure 12: Illustration of the difference in colour intensity achieved in the "floc colour" test.

Although the “floc colour” test was inconsistent with the geosmin adsorption capacity, PAC A produced a noticeably darker colour than any of the other ten PAC samples tested and in terms of ranking, was definitely placed first. It would appear as if flocculated material was covered with PAC for this carbon, whereas the PAC was covered with flocculated material in the case of other carbons. It was suspected that the floc colour was a function of zeta potential and/ or surface chemistry, which may result in the PAC being covered by flocculated material in some cases. A PAC that will be enmeshed into flocculated material might display a lower geosmin adsorption capacity due to interference with the transport process. No relationship was found between zeta potential and geosmin adsorption capacity (**Figure 13**). The correlation improves if the outlying data point is excluded from the data set, but is still not good enough to prove any correlation between zeta potential and geosmin adsorption capacity.

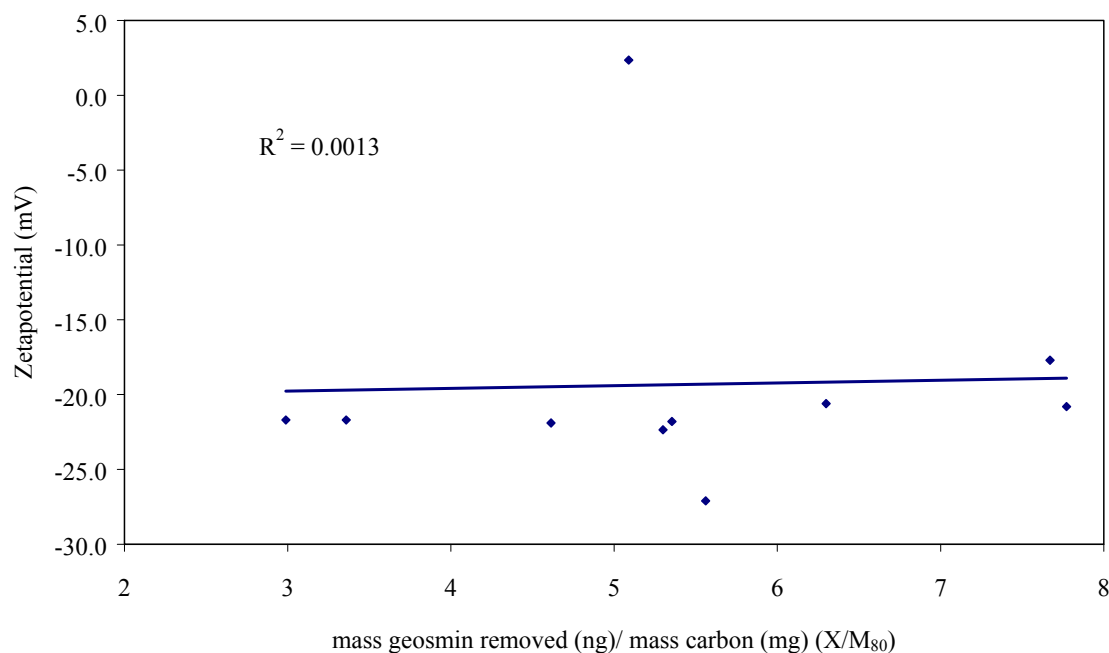


Figure 13: Relationship between the zeta potential and geosmin adsorption capacity.

Table 26: A comparison of the zeta potential values for the ten PAC samples.

PAC	X/M ₈₀ (ng geosmin removed/mg carbon)	Zeta potential (mV)
M	7.8	-20.8
A	7.7	-17.7
T	6.3	-20.6
I	5.6	-21.8
U	5.4	-21.8
D	5.3	-22.4
O	5.1	2.4
F	4.6	-21.9
R	3.4	-21.7
P	3.0	-21.7

PAC A and PAC F were subjected to XPS-analyses as examples of carbons with a high and low geosmin adsorption capacity respectively. The objective was to find relative differences in the concentration of the surface oxide groups in an attempt to explain the differences in “floc colour”. It was hoped that this data might shed some light on the activated carbon properties that are required for a carbon to have a high geosmin adsorption capacity. According to the literature, the main graphitical peaks on the surface of activated carbon appear at 284,6 eV, with three other more minor peaks appearing at 286,2, 287,6 and 289,1 eV respectively. The analyses of PAC A and PAC F were aligned to the main peak at 284,6 eV, which resulted in the three other peaks appearing at 285,7, 288,7 and 291,0 eV respectively. No significant differences between the surface oxide groups of PAC A and PAC F were detected by the analyst and the small differences that did exist between the two carbons were ascribed to sample preparation and not to surface chemistry (**Figure 14** and **Figure 15**). It was therefore decided not to perform XPS analyses on the other carbon samples as the analyses of PAC A and PAC F did not offer any explanation for the “floc colour” differences or differences in geosmin adsorption capacity. PAC F did not show any interparticle bonding during the preparation of the sample for XPS analysis and presented some difficulties during the XPS analysis. Enough sample was however analysed and the result would not have been any different for PAC F, even if it had showed similar interparticle bonding to PAC A. No explanation could be offered for the lack of interparticle bonding observed with PAC F.

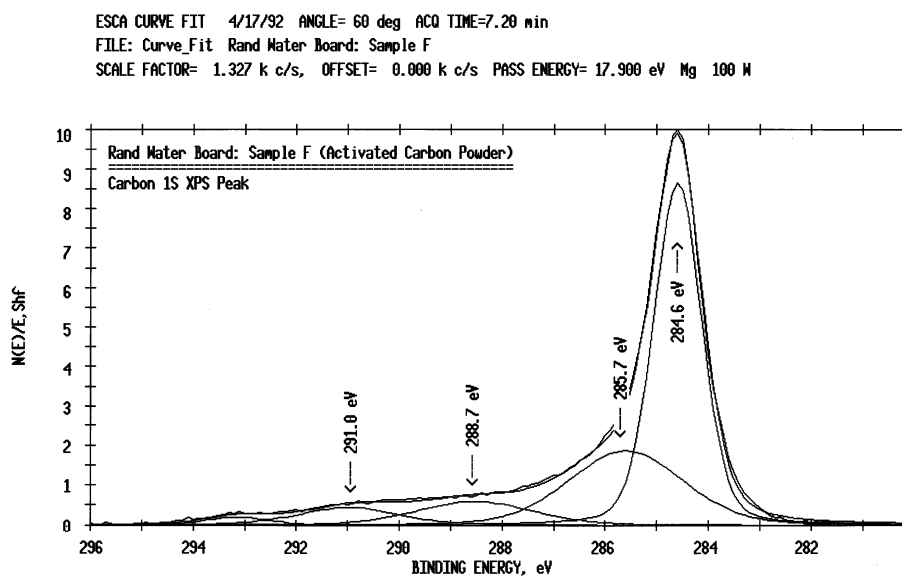


Figure 14: XPS analyses of PAC A.

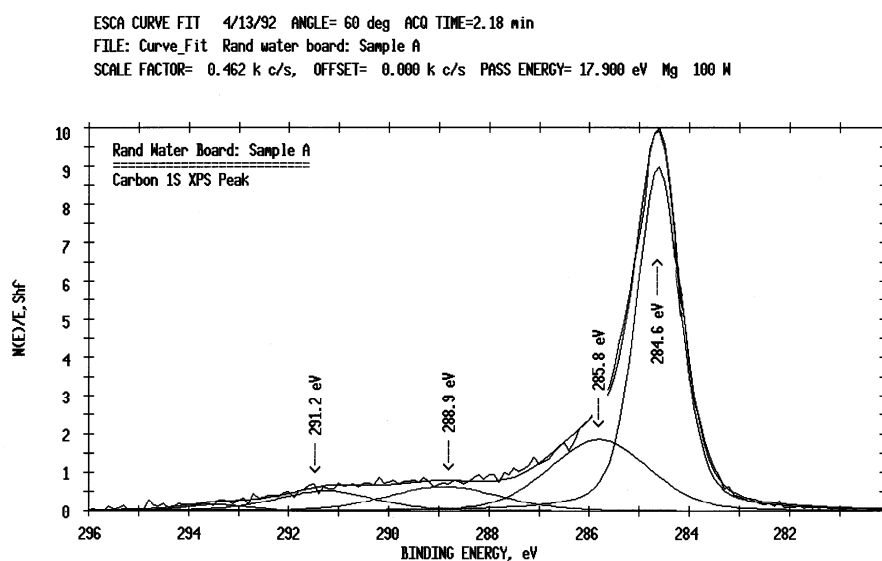


Figure 15: XPS analyses of PAC F.

The subjective and qualitative nature of the rating of the “floc colour” test were recognised by personnel at the Cape Metropolitan Council and attempts were made to quantify the measurement as described in paragraph 3.6 with the absorbance test at 850 nm. It is however not postulated that the 850 nm would measure “floc colour” and any correlations between the rating from the “floc colour” test and the absorbance (850 nm) of the flocculated matter

should not be ascribed to a relationship between the two parameters, as no scientific basis exists to prove such a relationship. A correlation between the 850 nm absorbance measurements and geosmin removal capacity was observed in initial experiments at the Cape Metropolitan Council. The 850 nm absorbance experiments were also performed at the laboratories of Rand Water and Umgeni Water using their respective methods for evaluating PAC with the different waters and flocculants (**Table 27 and Table 28**).

Table 27: 850 nm absorbance of the flocculated material tested at Rand Water.

PAC Sample	% Geosmin removed	850 nm Absorbance	“Floc test” rating
R1	77	1.453	1 (Darkest)
R2	49	0.7674	2
R3	37	0.6611	3

Table 28: 850 nm absorbance of the flocculated material tested at Umgeni Water.

PAC Sample	Effectiveness rating based on geosmin removal	850 nm Absorbance	Eye rating
U1	1 (Best PAC)	0.5954	1 (Darkest)
U3	2	0.4027	2
U4	3	0.2644	3
U2	4	0.1030	4

The 850 nm absorbance measurement was performed as a standard test in conjunction with the geosmin adsorption test at the Cape Metropolitan Council for 43 different PAC types. The relationship between the 850 nm absorbance measurement and the geosmin adsorption capacity is graphically displayed in **Figure 16**. The correlation between the 850 nm absorbance and geosmin adsorption capacity is believed to be a useful indicator, but not strong enough to be recommended as a test method for the screening and selection of PAC samples.

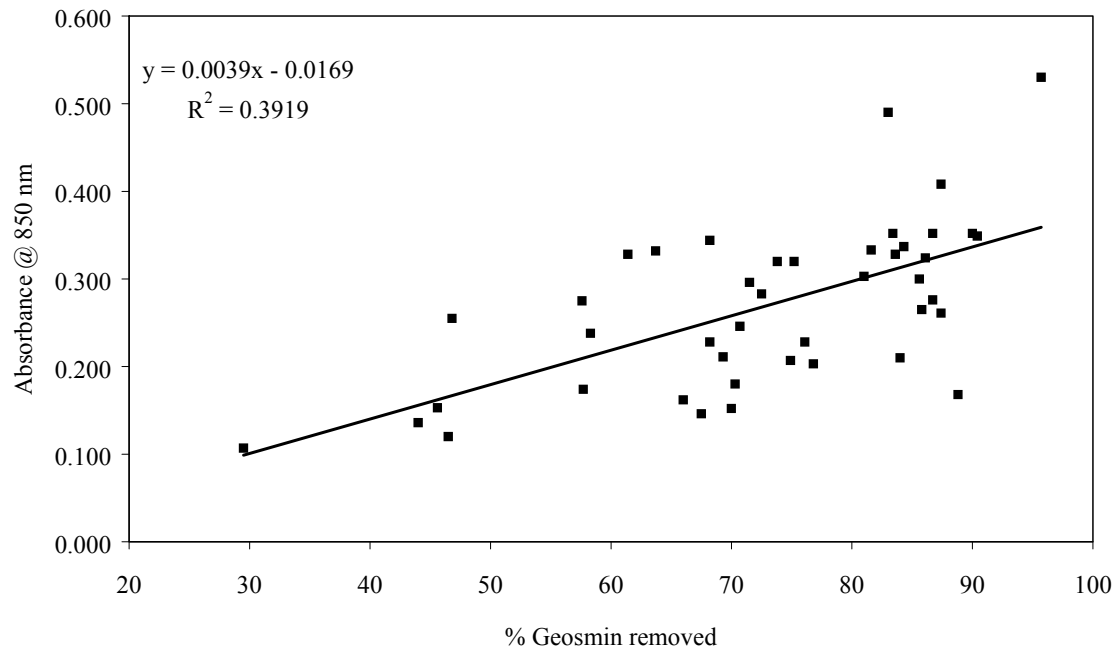


Figure 16: Graphical representation of the correlation between the 850 nm absorbance measurement and geosmin adsorption capacity.

CONCLUSIONS

The following conclusions were drawn from the work done on this project : -

- When ranking PAC's in order of geosmin removal efficiency there was no correlation between geosmin adsorption and the raw material used to manufacture the carbon (wood, coal, or coconut).
- The particle size of the PAC influences adsorption kinetics. Smaller particles generally have a higher adsorption rate than larger particles. However a practical limit exists for fine particles as they can penetrate through rapid sand filters.
- No correlation could be found between the pore volume of a carbon (whether micro-, meso-, or macro-) and its geosmin removal capability.
- An rough inverse trend was noted between tannin number and geosmin removal but no other correlations were observed between geosmin adsorption capacity and the carbon adsorption numbers or the physical characteristics of the carbon.
- The geosmin adsorptive capacity of PAC is not affected by the presence of 2-MIB.
- Significantly higher PAC dosages are required for 80% 2-MIB removal than for 80% geosmin removal.
- There is good positive linear correlation between microcystin-LR adsorption capacity and geosmin adsorption capacity.
- Water quality has an effect on geosmin removal by PAC. Deionised water gives best results, river waters were intermediate, and spent filter washwaters gave worst results. This was attributed to enmeshing of PAC in the suspended material in the water.

- Geosmin removal was also dependent on the nature of the water treatment process. The best PAC performance (lowest dosages) was when treating with slaked lime and polyelectrolyte. A slightly higher dosage was needed for polyelectrolyte alone, and highest dosages were necessary when using activated silica (from sodium silicate).
- PAC rankings by two other water treatment authorities (Cape Metropolitan Council and Umgeni Water) were very similar to Rand Water's results when tested on local waters using in-house evaluation methods. This indicates that the holding of one centralised PAC stock for use by various authorities is feasible.
- The relationship between 4-nitrophenol removal and geosmin removal for a particular PAC gave an inverse trend but the correlation coefficient was poor.
- No relationship was found between zeta potential and the geosmin adsorption capacity of a particular PAC.
- The quick estimation procedure developed by Cape Metropolitan Council comprising visual colour ratings or absorption on a spectrophotometer at 850 nm gave a reasonable indication of the geosmin removal potential of a PAC but was not infallible.

RECOMMENDATIONS FOR FUTURE STUDIES

- A research project could be undertaken in collaboration with PAC manufacturers to try to establish the conditions under which the manufacturing processes would be successful in producing a PAC with high geosmin/ 2-MIB adsorption capacity. The finer details of the manufacturing process are not disclosed to water authorities and are usually regarded as trade secrets that would give the manufacturer a competitive advantage. This competitive advantage does not exist since no manufacturer knows the ideal conditions under which a PAC is formed with high geosmin/ 2-MIB absorbing capacity.
- The present project did not produce a simple and cost effective procedure to evaluate PAC for geosmin/ 2-MIB removal. More work could be undertaken on this topic.

TECHNOLOGY TRANSFER

The findings of this project have not been published up to date and it would be envisaged that a publication in a scientific journal could be part of the technology transfer process. An information session could also be held for the benefit of smaller municipalities to transfer knowledge on PAC selection procedures.

APPENDICES

ADSORPTION ISOTHERMS OF GEOSMIN ADSORPTION ONTO PAC (FIGURES 17 TO 26)

PAC M

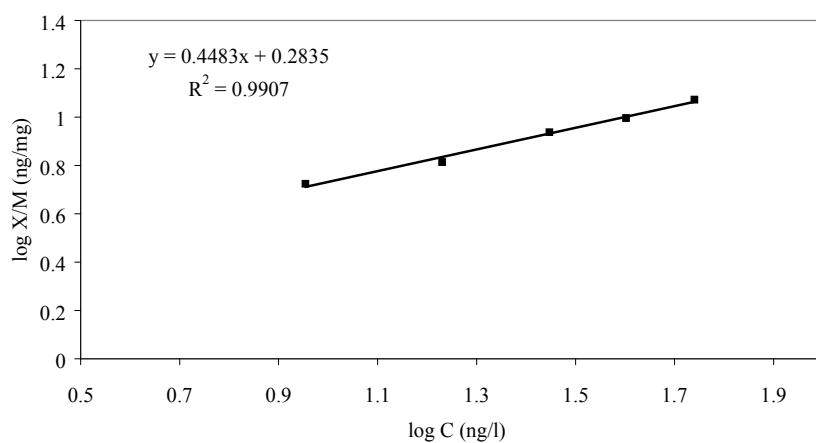


Figure 17: Adsorption isotherm of geosmin onto PAC M.

PAC A

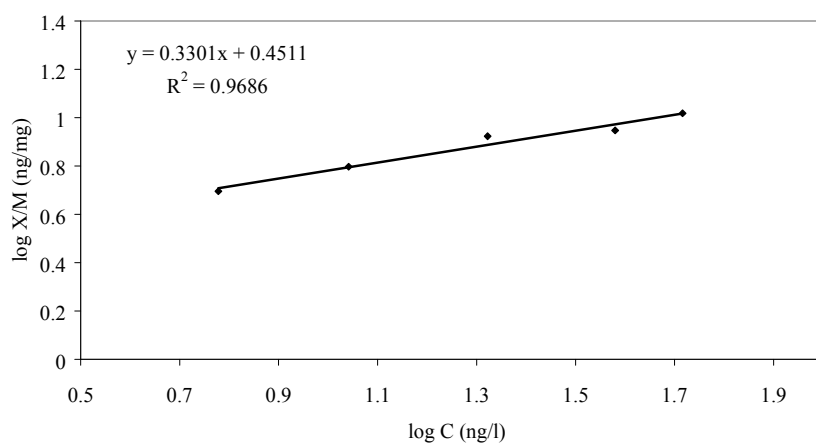
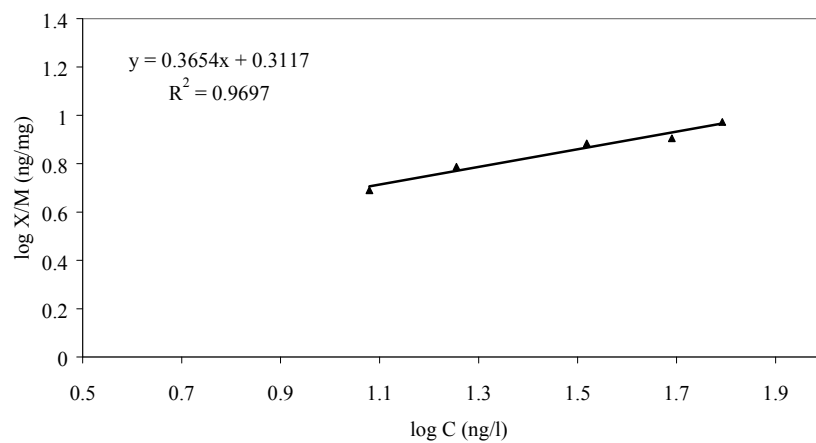
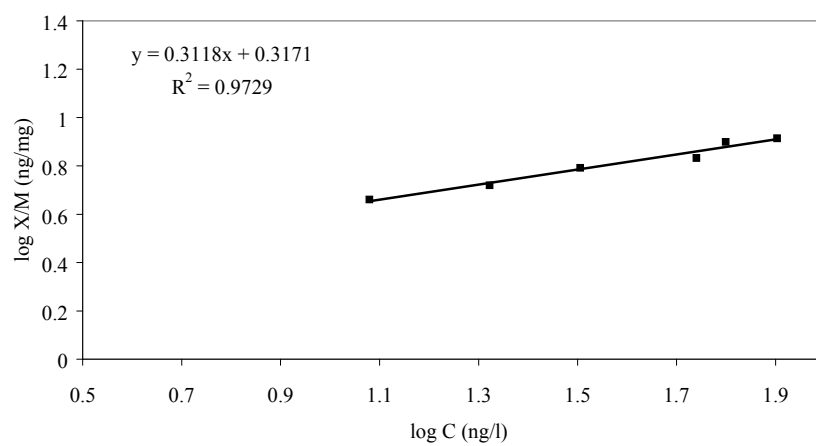
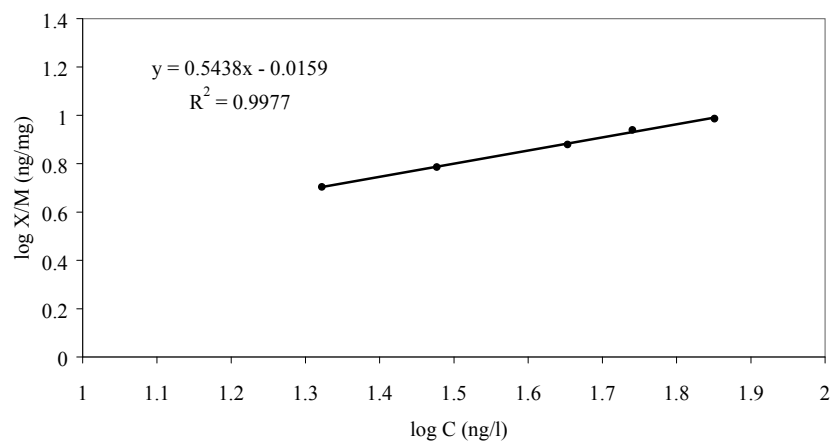
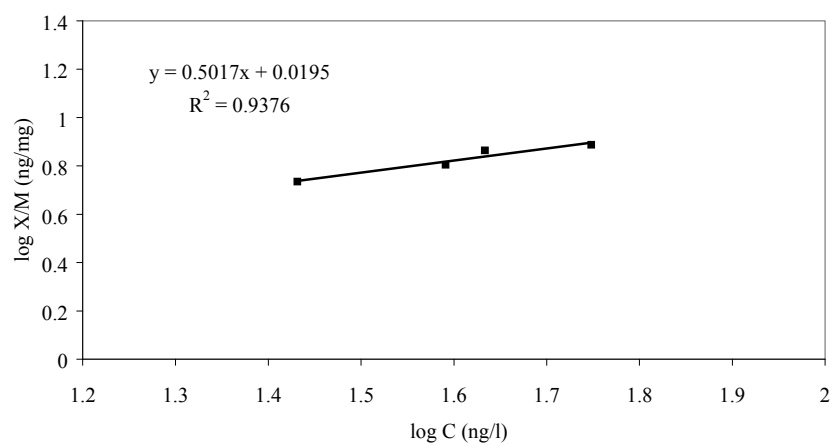
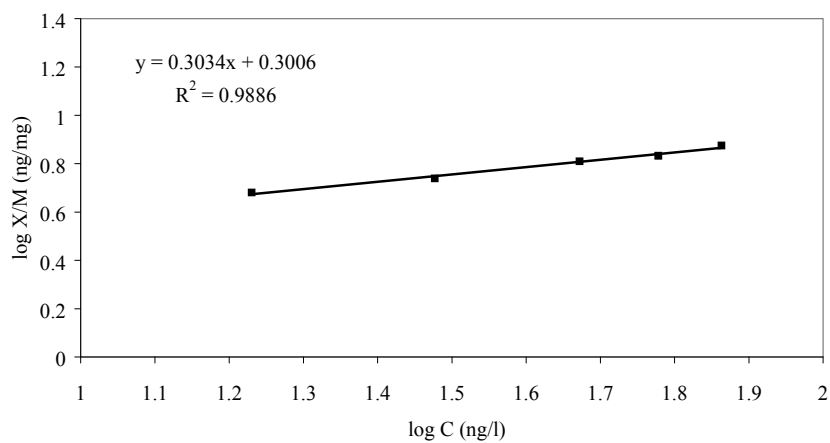
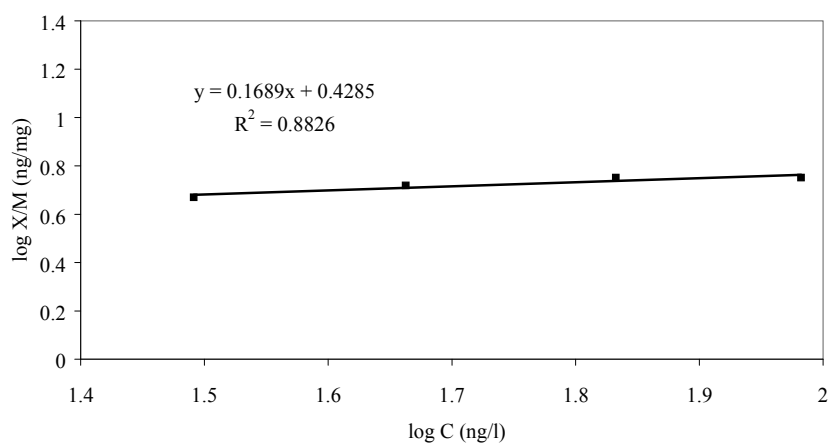
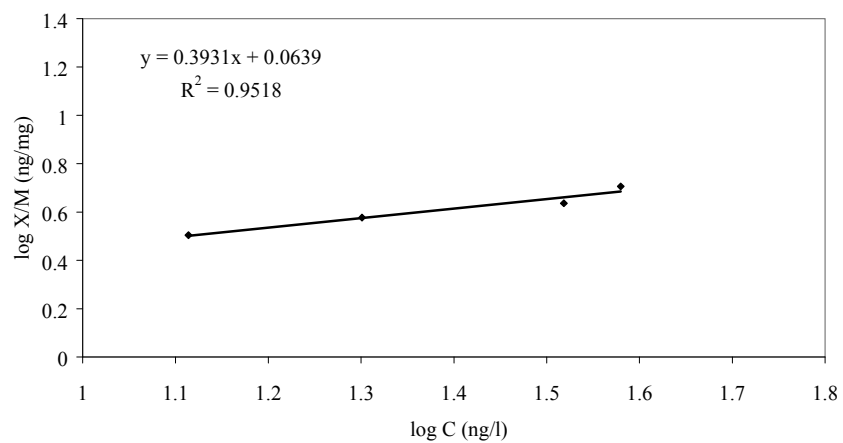
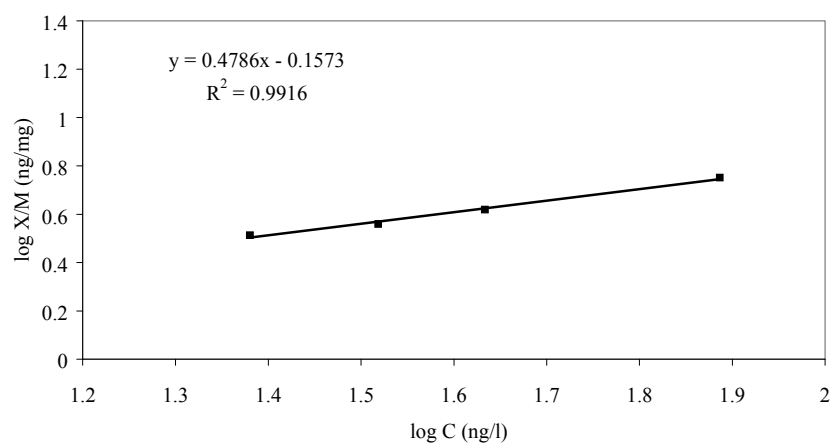


Figure 18: Adsorption isotherm for geosmin onto PAC A.

PAC T**Figure 19:** Adsorption isotherm for geosmin onto PAC T.**PAC I****Figure 20:** Adsorption isotherm for geosmin onto PAC I.

PAC U**Figure 21:** Adsorption isotherm for geosmin onto PAC U.**PAC D****Figure 22:** Adsorption isotherm for geosmin onto PAC D.

PAC O**Figure 23:** Adsorption isotherm for geosmin onto PAC O.**PAC F****Figure 24:** Adsorption isotherm for geosmin onto PAC F.

PAC R**Figure 25:** Adsorption isotherm for geosmin onto PAC R.**PAC P****Figure 26:** Adsorption isotherm for geosmin onto PAC P.

ADSORPTION ISOTHERMS OF 2-MIB ONTO PAC (FIGURES 27 AND 28)

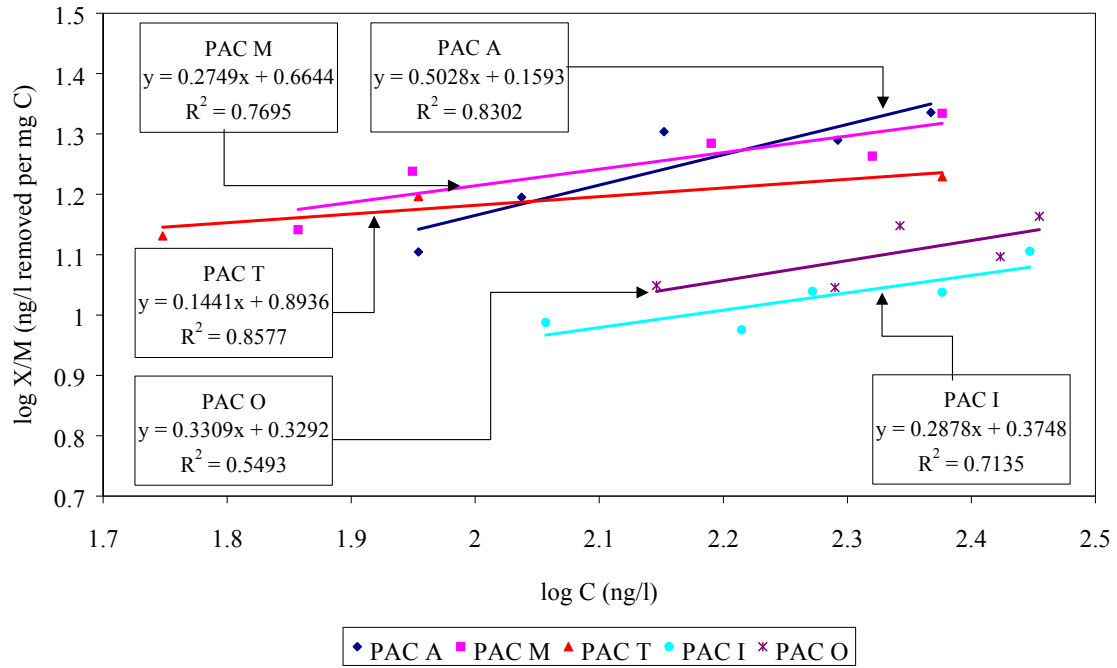


Figure 27: Adsorption isotherm of 2-MIB in the presence of geosmin for five PAC's.

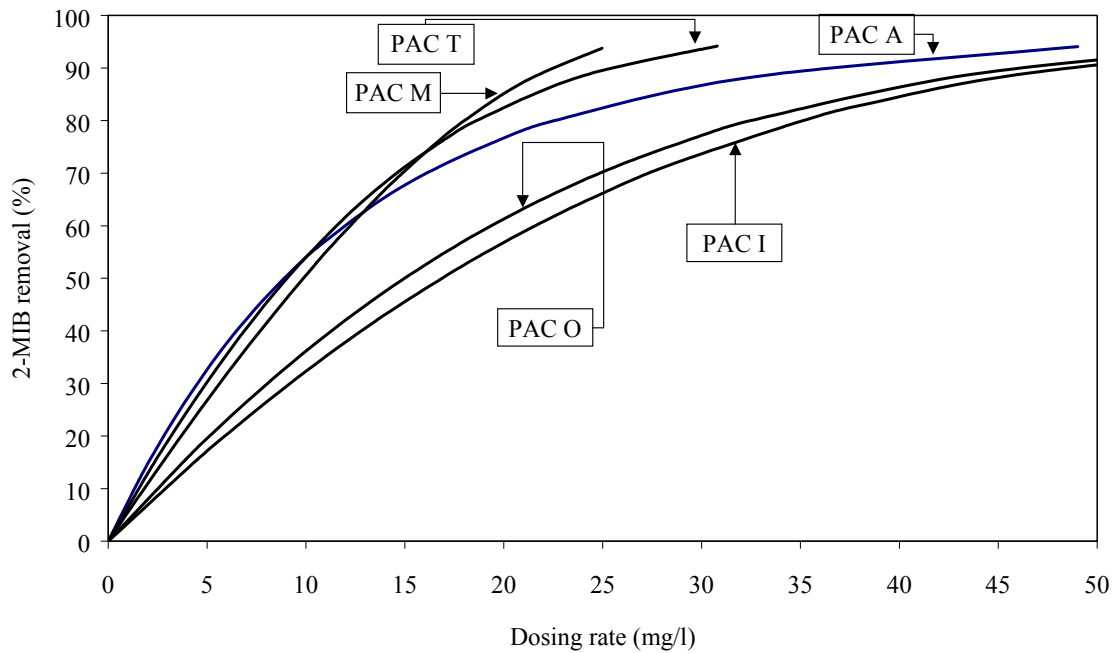


Figure 28: Removal of 2-MIB as a function of PAC dosage for five carbons.

INFLUENCE OF DIFFERENT COAGULANTS ON THE ADSORPTION ISOTHERMS OF PAC (FIGURES 29 AND 30)

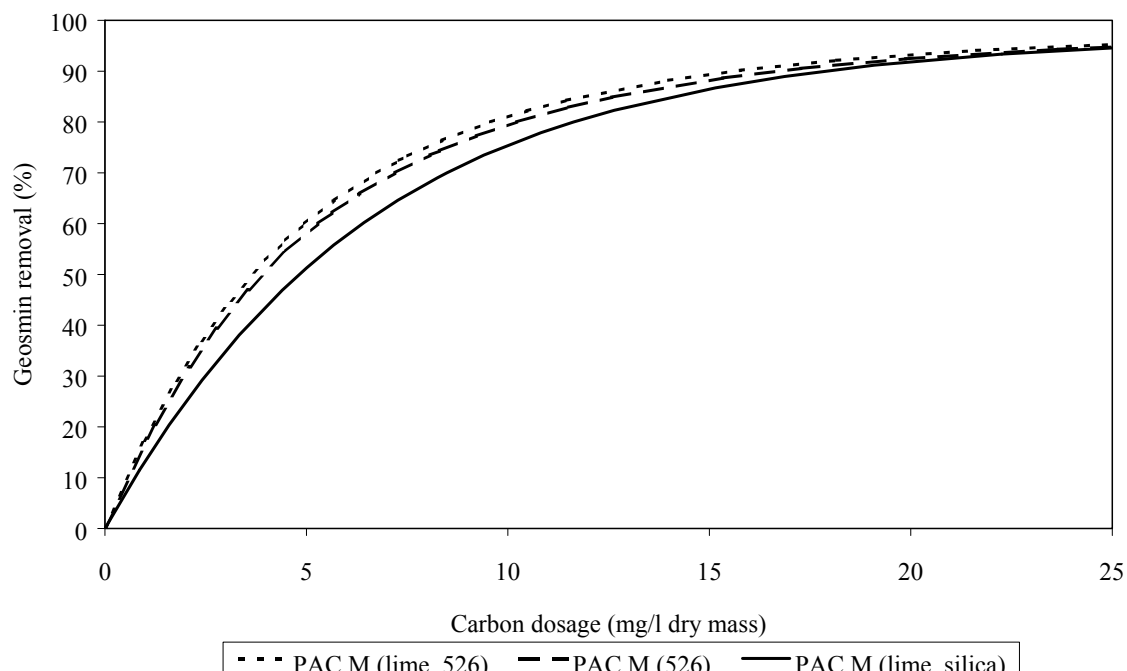


Figure 29: Influence of different coagulants on the adsorption isotherm of PAC M

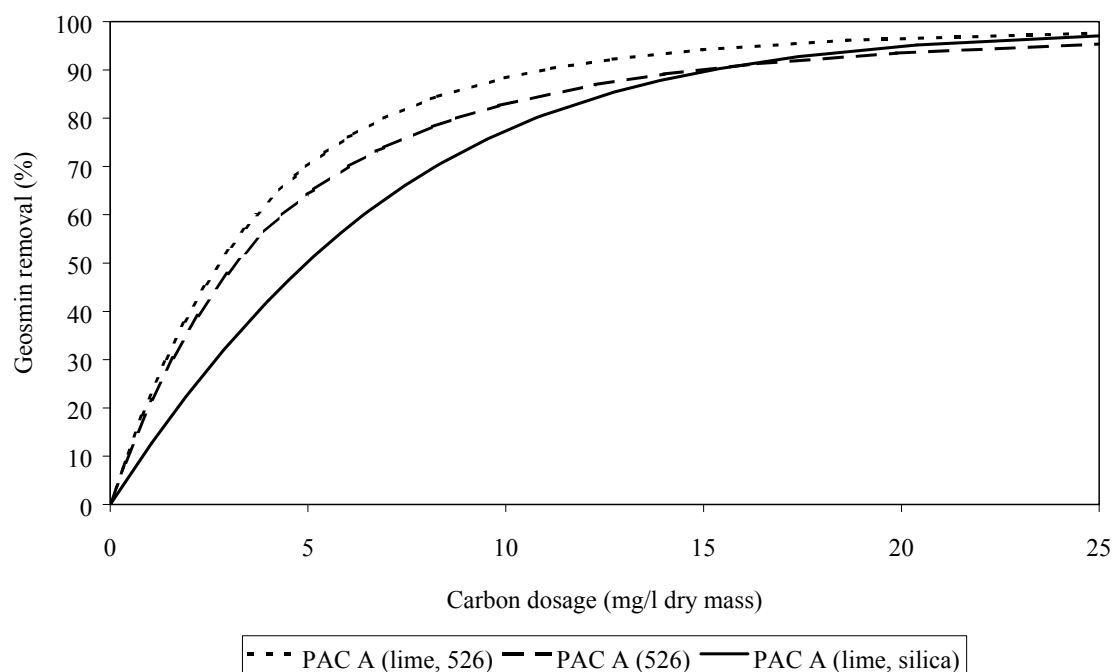


Figure 30: Influence of different coagulants on the adsorption isotherm of PAC A.

ADSORPTION ISOTHERMS FOR 4-NITROPHENOL ONTO PAC (FIGURES 31 to 40)

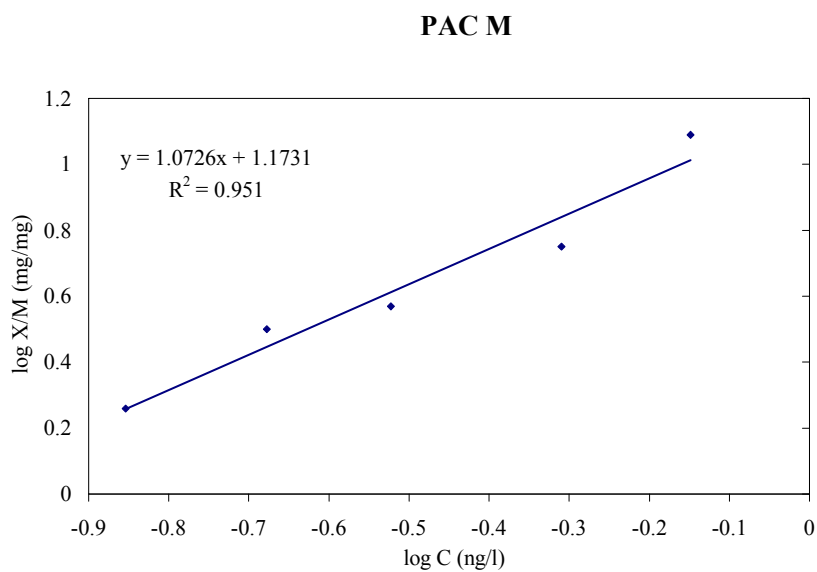


Figure 31: Adsorption isotherm for 4-nitrophenol onto PAC M.

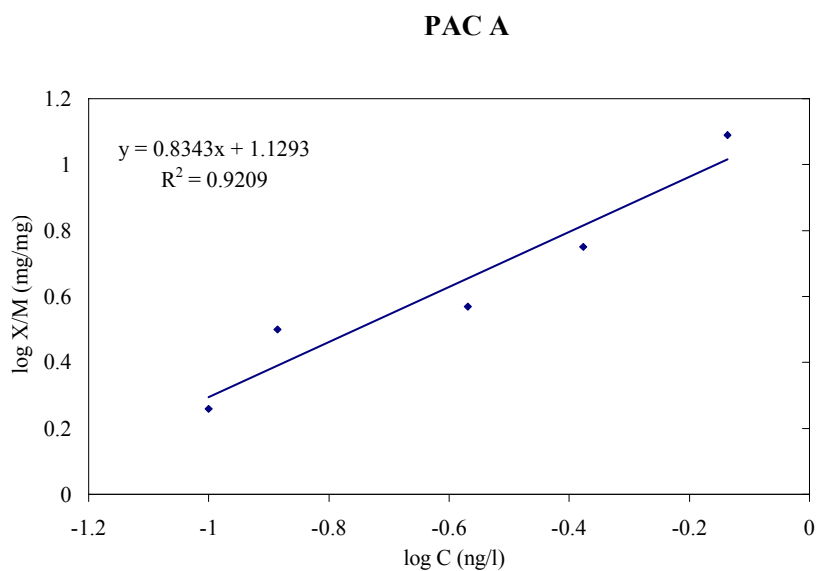
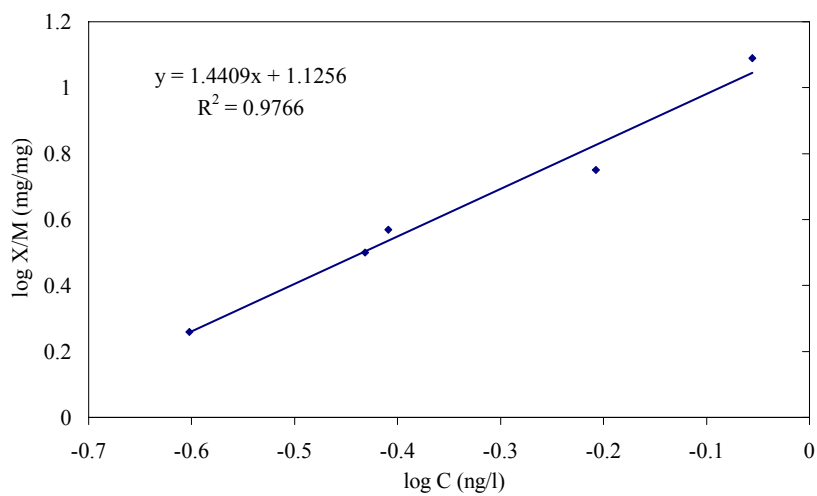
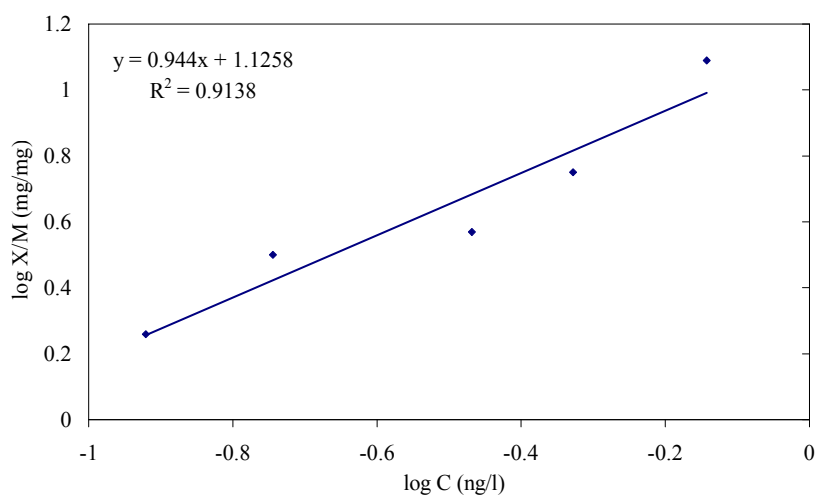
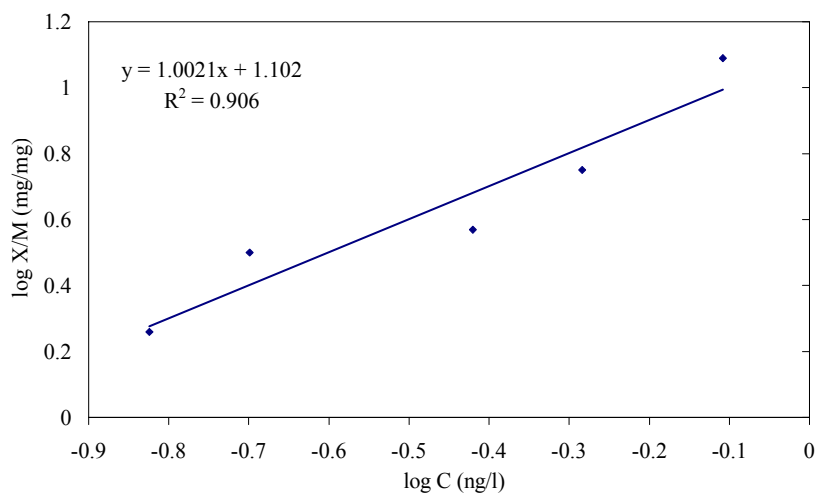
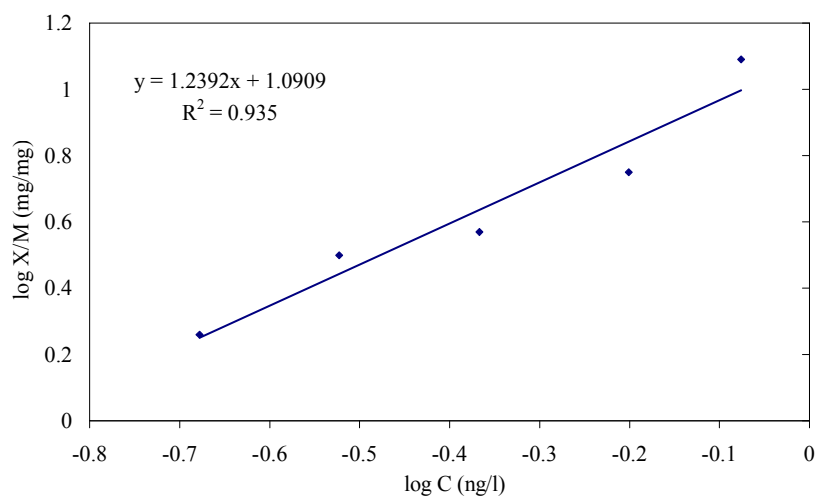
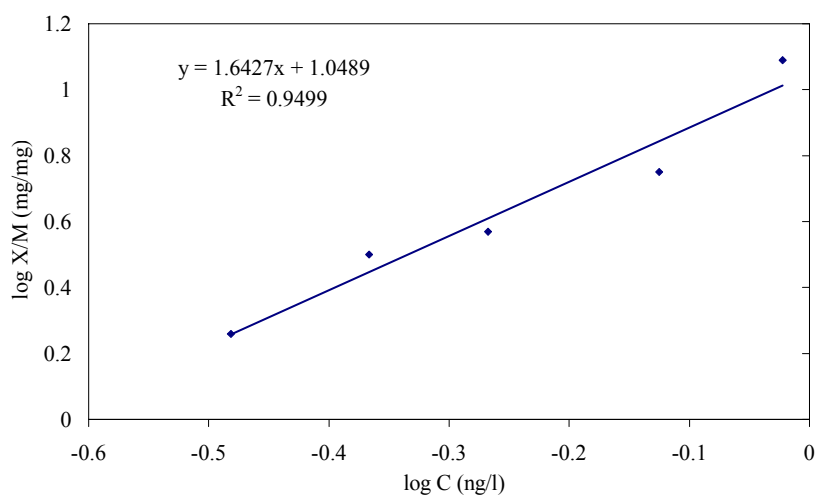
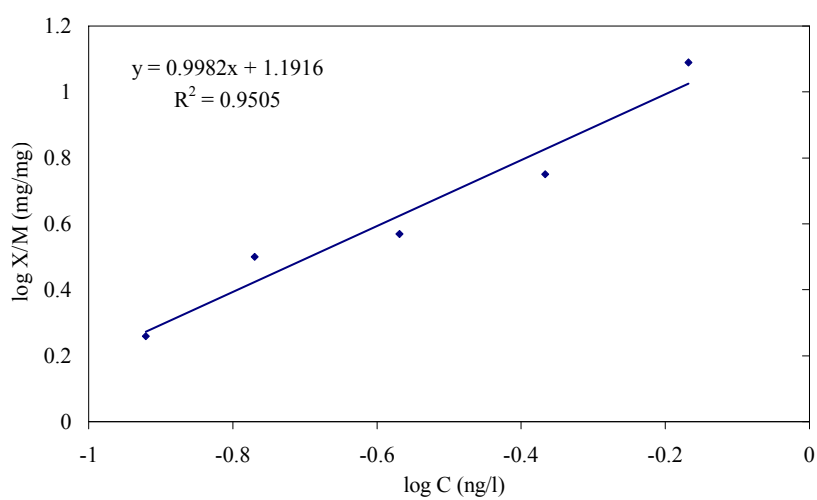
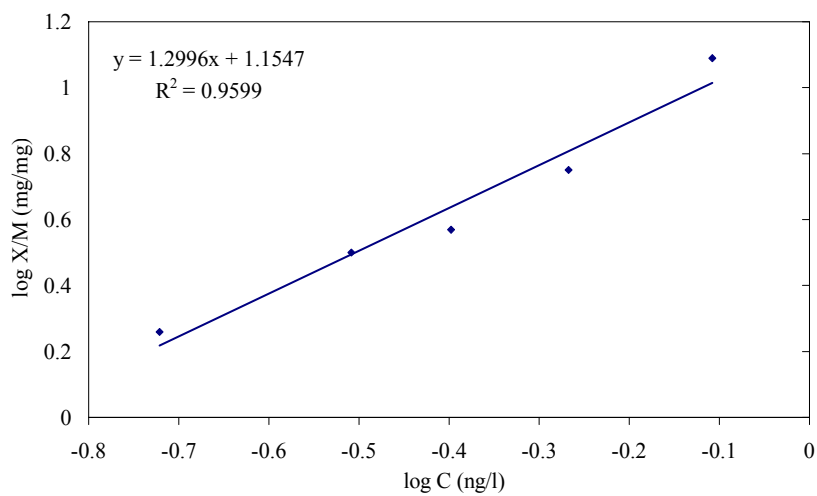
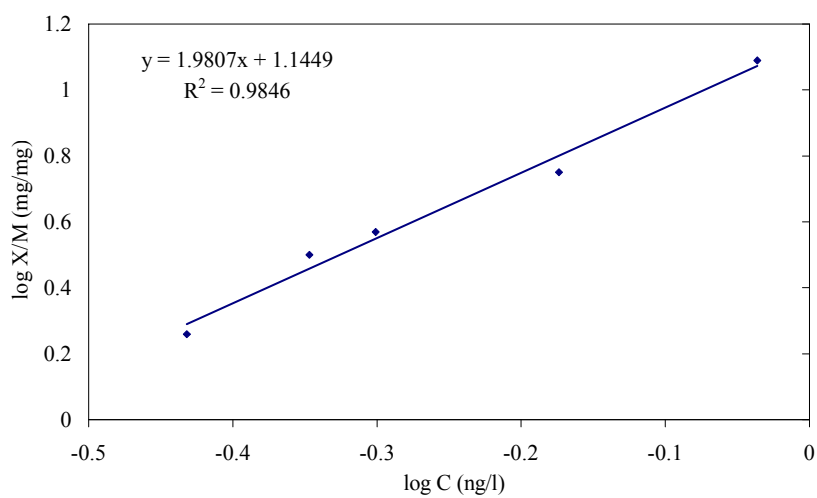


Figure 32: Adsorption isotherm for 4-nitrophenol onto PAC A.

PAC T**Figure 33:** Adsorption isotherm of 4-nitrophenol onto PAC T.**PAC I****Figure 34:** Adsorption isotherm of 4-nitrophenol onto PAC I.

PAC U**Figure 35:** Adsorption isotherm of 4-nitrophenol onto PAC U.**PAC D****Figure 36:** Adsorption isotherm of 4-nitrophenol onto PAC D.

PAC O**Figure 37:** Adsorption isotherm of 4-nitrophenol onto PAC O.**PAC F****Figure 38:** Adsorption isotherm of 4-nitrophenol onto PAC F.

PAC R**Figure 39:** Adsorption isotherm of 4-nitrophenol onto PAC R.**PAC P****Figure 40:** Adsorption isotherm of 4-nitrophenol onto PAC P.

REFERENCES

1. Persson P., Sensory Properties and Analysis of two Muddy Odour Compounds, Geosmin and 2-methylisoborneol, in Water and Fish, *Wat Res*, 1980, vol. 14, 1113–1118.
2. Bowmer K.H., Padovan A., Oliver R.L. & Ganf G.G., Physiology of Geosmin Production by *Anabaena Circinalis* Isolated from the Murrumbidgee River, Australia, *Wat. Sci. Tech.*, 1992, vol. 25(2), 259–267.
3. Hayes K.P. & Burch M.D, Odorous Compounds Associated with Algal Blooms in South Australian Waters, *Wat Res*, 1980, vol. 23(1), 115–121.
4. Montiel A.J., Municipal Drinking Water Treatment Procedures for Taste and Odour Abatement – A Review, *Wat. Sci. Tech.*, 1983, vol. 15, 279-289.
5. Lalazary S. *et al.*, Oxidation of five earthy-musty taste and odour compounds, J. AWWA, 1986, vol. 78(3), 62.
6. Meintjies E., Geosmin: It Stinks, WISA 1996 Proceedings.
7. Ando A., Miwa M., Kajino M. & Tatsumi S., Removal of Musty-Odoriferous Compounds in Water and Retained in Algal Cells through Water Purification Processes, *Wat. Sci. Tech.*, 1992, vol 25(2), 299-306.
8. Internal Rand Water Report, “**The Control of Off-Flavours in Drinking Water**”, File no. 193/0, Memorandum no. 08/97/13, 1997.
9. Bruce D., Westerhoff P. & Brawley-Chesworth A., Removal of 2-methylisoborneol and Geosmin in Surface Water Treatment Plants in Arizona, *J. Wat. Suppl.: Res and Tech.*, 2002, vol. 51(4), 183-197.
10. Lalezary S., Pirabazari M., McGuire M.J. & Krasner S.W., Air Stripping of Taste and Odor Compounds from Water, *J. AWWA*, 1984, vol. 76, 83-86.
11. Lalezary S., Pirabazari M. & McGuire M.J., Oxidation of Five Earthy-Musty Taste and Odour Compounds, *J. AWWA*, 1986, vol. 78 (3), 62-69.

12. Chudyk W.A., Snoeyink V.L., Beckmann D. & Temperly T.J., Activated Carbon Versus Adsorption of 2-methylisoborneol and Chloroform, *J. AWWA*, 1979, vol. 71, 529-538.
13. Najm I.N., Snoeyink V.L., Lykins Jr B.W. & Adams J.Q., Using Powdered Activated Carbon: A Critical Review, *J. AWWA*, 1991, vol. 83, 65-76.
14. American Water Works Association (AWWA), Standard for Powdered Activated Carbon ANSI/AWWA B600-90, USA, 1991.
15. Ruthven D.M., “**Principles of Adsorption and Adsorption Processes**”, Joshn Wiley & Sons, New York, 1984, 7.
16. Holden M.J., Manufacture and Uses of Activated Carbon, *Effluent and Water Treatment Journal*, 1982, 27-46.
17. Greenbank A.I., Effects of Starting Material on Activated Carbon Characteristics and Performance in Water Treatment, Poster presented at the Brewing Congress of the Americas (BCOA), St Louis, MO, 1992.
18. IUPAC Compendium of Chemical Terminology (2000), <http://www.chemsoc.org/chembytes/goldbook/> [2002, June 3].
19. Cheremisinoff P.N., Ellerbusch F., **Carbon Adsorption Handbook**, Ann Arbor Science Publishers Inc., Michigan, 1980, 57.
20. Lalezary S., Pirbazari M., and McGuire M.J., “Evaluating Activated Carbons for Removing Low Concentrations of Taste- and Odour-Producing Organics”, *Journ. AWWA*, 1986, vol. 79, 76.
21. Huang C., Van Benschoten J.E. & Jensen J.N., Adsorption kinetics of MIB and geosmin, *J. AWWA*, 1996, vol. 88, 116-128.
22. Knappe D.R.U., Matsui Y., Snoeyink V.L., Roche P., José Prados M. & Bourbigot M., Predicting the Capacity of Powdered Activated Carbon for Trace Organic Compounds in Natural Waters, *Environ. Sci. Technol.* 1998, vol. 32, 1694-1698.
23. Najm I.N., Snoeyink V.L., Suidan M.T., Lee C.H. & Richard Y., Effect of Particle Size and Background Natural Organics on the Adsorption Efficiency of PAC, *J. AWWA*, 1990, vol. 82, 65-72.

24. Crittenden J.C., Luft P. & Hand D.W., Prediction of Multicomponent Adsorption Equilibria in Background Mixtures of Unknown Composition, *Water Res*, 1985, 19(12), 1537.
25. Najm I.N., Snoeyink V.L. & Richard Y., Effect of Initial Concentration of an SOC in Natural Water on Its Adsorption by Activated Carbon, *J. AWWA*, 1991, vol. 83(5), 57.
26. Gillogly T.E.T., Snoeyink V.L., Newcombe G. & Elarde J.R., A Simplified Method to Determine the Powdered Activated Carbon Dose Required to Remove Methylisoborneol, *Wat. Sci. Tech.*, 1999, vol. 40(6), 59-64.
27. Kozlowski C. & Sherwood M.A., X-Ray Photoelectron Spectroscopic Studies of Carbon-fibre Surfaces, *J. Chem Soc., Faraday Trans. 1*, 1984, 80, 2099-2107.
28. Mamgun C.L., Benak K.R., Daley D.A. & Economy J., Oxidation of Activated Carbon Fibres: Effect on Pore Size, Surface Chemistry, and Adsorption Properties, *Chem. Mater.*, 1999, 11, 3476-3483. Persson P., Sensory Properties and Analysis of two Muddy Odour Compounds, Geosmin and 2-methylisoborneol, in Water and Fish, *Wat Res*, 1980, vol. 14, 1113–1118.