SUPERCRITICAL FLUID REGENERATION OF EXHAUSTED GRANULAR ACTIVATED CARBON–POTENTIAL APPLICATION TO WATER PURIFICATION

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REPORT TO THE WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

Activated carbon, a material with excellent adsorption capability, is used, among other applications, in water purification processes for the removal of organic substances. For economical reasons activated carbon is regenerated rather than discarded once the adsorbing surface is exhausted. Until now, surface recovery has been achieved mainly by thermal regeneration, with the disadvantages of high energy demand, micropore burn-out and carbon mass loss. Other possibilities include chemical and biological regeneration, but these methods are applicable in a few special cases only.

During recent years supercritical fluid extraction proved to be a potential alternative method for the regeneration of exhausted activated carbon. Promising experiments have been performed with samples of activated carbon exhausted under clinical laboratory conditions. In this study samples were investigated which had been exhausted under "real-world" conditions in water purification installations in southern Africa. The objectives were to attempt the regeneration of such samples with supercritical carbon dioxide (*sc*-CO_2), to optimise the regeneration with regard to the adjustable parameters controlling the limiting processes and to gain insight into the mechanism of supercritical fluid regeneration.

The excellent adsorption properties of activated carbon stem from a large surface area of up to 1 500 m^2/g. A surface area of this dimension is obtained in the manufacture of activated carbon by subjecting all conceivable forms of carbonaceous material (wood, coal, nut shell) to high temperatures and thus transforming it into a labyrinth-like pore structure. Especially organic substances are adsorbed onto this active surface either by van der Waals forces (physisorption) or by chemical bonds (chemisorption). Activated carbon is classified according to the type of raw material, the magnitude of the

surface area, the size, shape, density and hardness of the particles and the nature of the pore structure.

The properties of gases under supercritical conditions (31 °C and 73 bar for CO_2) are considered ideal to extract substances from a solid matrix as is required for the regeneration of exhausted activated carbon. These supercritical fluids exhibit densities similar to those of liquids (high solvent strengths) and diffusion coefficients similar to those of gases (excellent transport characteristics), enabling them to effectively dissolve and/or desorb contaminants from the carbon surface and to easily enter/exit even the smallest pores and carry away any released material. On restoring ambient conditions, the supercritical fluid is reconverted into a gas and all formerly dissolved/desorbed substances fall out instantly.

The samples investigated were obtained from water purification plants situated in Windhoek (Namibia), at Vereeniging (South Africa) and in Durban (South Africa). The selection was based, on the one hand, on the different raw water types and operational conditions at the respective installations in order to acquire a representing overview and, on the other hand, on the common type of GAC used at these installations in order to exclude type of carbon as a variable affecting the regeneration.

The regeneration runs on the spent activated carbon samples were performed with a bench-top supercritical fluid extractor featuring a microprocessor controlled system for *sc*-CO_2 at temperatures of up to 150 °C and pressures ranging between 130 and 450 bar, and a temperature controlled variable flow restrictor for the reinstatement of ambient conditions and the collection of the extracted substances.

The extent of regeneration of all samples was monitored in terms of a titrimetrically determined iodine number based on milligram of iodine adsorbed per gram of activated carbon. Since the adsorbed amount of iodine depends on the available active carbon surface, it was possible to correlate surface recovery during regeneration with a corresponding increase in iodine number.

A statistical method based on surface response analysis was utilised to design a minimum of ten experimental runs for each sample by which the temperature and pressure dependence of the regeneration at a fixed flow rate (2 ml/min) and extraction time (10 to 90 minutes) could be determined. The resulting three-dimensional surface response graphs revealed that a pressure of 450 bar and a temperature of 150 °C are optimum parameter values for the supercritical fluid regeneration in all cases and that both desorption of substances from the carbon surface and dissolution of substances in the *sc*-CO_2 play a role in the regeneration process. The species removed from the carbon surface were not analysed since an identification of all possible types of contaminants and their respective influence on the studied regeneration process were considered beyond the scope of this investigation.

The samples selected for investigation were all "real-world" samples, in contrast to clinical samples purposively exhausted for the majority of studies on the regeneration of activated carbon by other researchers.

These clinical samples are exhausted in a laboratory under ideal conditions with a limited number of contaminants in high concentration. The exhaustion features low-energy adsorption and capillary condensation, with the result that regeneration is fairly easy. For "real-world" samples the exhaustion comprises the adsorption of different contaminants in minute concentrations over an extended period of time, so that the subsequent desorption process is complicated by high-energy demand, possible biological growth and ageing of the adsorbed species. The differentiation between these two types of samples is important to fully understand the regeneration results for the samples investigated.

The samples obtained from Durban were activated carbon which had not been subjected to any kind of regeneration. These were exhausted over a period of 18 months while being utilised to purify weakly polluted surface water and were therefore strictly "real-world" samples. The *sc*-CO_2 regeneration of these samples was disappointing (2-5% recovery of active surface only), probably as a result of ageing of the adsorbed species, the varying environmental conditions and possible microbial surface growth.

The samples obtained from Vereeniging were exhausted only for about 100 hours by purifying highly concentrated filter backwash water. These samples had not been regenerated before and closely resembled samples clinically exhausted in a laboratory. The *sc*-CO_2 extraction performed at optimum parameter values resulted in an increase of up to 90% of the original active surface area, in agreement with results previously obtained for laboratory prepared samples.

The samples obtained from Windhoek had been previously regenerated thermally, as a result of which "dead" material had been burnt onto the active surface. The treatment with *sc*-CO_2 resulted in a significant mass loss (over 20%) due to the successful removal of a double layer of "dead" material, but without a significant increase in iodine number as a result of the destroyed active surface and micropore structure. It could thus be concluded that a prerequisite for supercritical fluid regeneration is that the activated carbon should not have been regenerated thermally before.

From the results of this investigation the requirements for the supercritical fluid regeneration of activated carbon exhausted in "real-world" water purification systems could be derived. These include that samples should not have been subjected to thermal regeneration before, that samples should be free of impeding biological growth and aged adsorbed species and that optimum supercritical conditions (high temperature for effective desorption, high density for guaranteed dissolution) should be selected.

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The Steering Committee responsible for the project consisted of the following persons:

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0. INTRODUCTION

Activated carbon has for long been recognised as one of the most versatile adsorbents for the effective removal of low concentrations of certain substances from solution. The use of charcoal, the forerunner of modern activated carbon, by ancient Egyptians for medical purposes and water purification dates back to 2000 BC [1].

The high adsorptive capacity of activated carbon, the main reason for its wide-spread utilisation, is attributed mainly to its highly porous structure, resulting in a relatively large surface area of up to 1 500 m^2/g. This renders activated carbon a suitable agent to support water purification processes for drinking water. Especially in South Africa, where water is a valuable natural resource, activated carbon finds increasing application [1-2].

In view of high manufacturing costs it is not economically viable to discard exhausted activated carbon. Thus a number of regeneration methods (thermal, chemical, biological) has been developed. However, these methods are either energy/cost intensive or environmentally threatening. As a consequence, supercritical fluid extraction (SFE) potentially offers an alternative method for the regeneration of exhausted activated carbon.

Preliminary research work showed the possibility to restore up to 92% of the original adsorption capacity of exhausted activated carbon by supercritical carbon dioxide (sc-CO_2) [3]. The samples investigated were artificial in the sense that they had been exhausted under laboratory conditions for the purpose of investigating the feasibility of supercritical fluid regeneration rather than for the purpose of simulating real samples employed in water purification. That work, and preliminary investigations by other authors worldwide, needed to be followed up by an investigation into the regeneration of activated carbon exhausted in "real-world" water purification installations where many additional factors might come into play.

This study was therefore aimed at attempting supercritical fluid regeneration of activated carbon exhausted in water purification processes employed in the southern Africa water fraternity. For a representative survey, activated carbon samples from water purification installations in Windhoek (Goreangab Reclamation Plant), at Vereeniging (Zuikerbosch Pumping Station and Barrage Water Purification Installation) and in Durban (Umgeni Water Process Evaluation Facility) were investigated. These were representative of installations for the production of drinking water from eutrophic surface water (Vereeniging), from fresh water containing industrial effluent, sewage and stormwater run-off (Windhoek) and from water characterised by bad odour and taste (Durban).

The envisaged study included performance of several runs for each sample, using an advanced benchtop supercritical fluid extractor under different conditions in the *sc*-CO_2 domain and within the limitations of the regeneration equipment. The extent of regeneration needed to be monitored in terms of iodine numbers determined by a standard titrimetric method and in terms of mass loss where applicable.

The accumulated extraction data could, once being processed and interpreted, be used to optimise the process efficiency and to obtain insight into the mechanism of removal of substances from the carbon surface.

Finally a comparison of the different types of samples from the various sites with regard to the viability of and prerequisites for successful supercritical fluid regeneration could be achieved.

1. ACTIVATED CARBON – A GENERAL OVERVIEW

The chemical properties of activated carbon are determined by functional groups on the surface which are formed during the activation process at lattice imperfections by conversion with atmospheric oxygen and hydrogen. The method of activation determines the nature of the functional groups to a large extent, of which the most important are those containing oxygen, called the surface oxides. One distinguishes between basic and acid surface oxides, which are able to influence both the pH of solutions and the selectivity of adsorption towards certain polar components in solution. Activated carbons used in water treatment are activated at temperatures between 500 and 900 °C.

1.1 Adsorption Capability

Adsorption is defined as the increase in concentration of a particular component on the surface of a solid material, e.g. activated carbon. The forces responsible for molecules to become adsorbed at a solid surface are similar to those causing a drop of water to have the smallest possible area, namely surface tension or surface free energy [4]. Since a solid can hardly vary its surface like a drop of water, adsorption needs to be accompanied by a decrease in free energy.

Adsorption processes may be classified as physical or chemical, depending on the nature of the forces involved. Physical adsorption, or physisorption, is caused by rather weak van der Waals forces, and the enthalpy of adsorption ΔH_{ads} is less then 40 kJ/mol and thus about two times larger than the enthalpy of condensation ΔH_{cond}. Chemical adsorption or chemisorption involves electron transfer and true chemical bonding between the adsorbate and the solid surface. Thus the enthalpy of adsorption ΔH_{ads} is in the range of the enthalpy of reaction ΔH_{react} of at least 80 kJ/mol. This explains why chemisorbed compounds cannot easily be desorbed from the surface of activated carbon [5].

The adsorption at the planar surfaces, which constitute most of the surface area (up to 1 500 g/m^2) and which are thus largely responsible for the adsorptive properties of activated carbon, is of a physical nature, though electrons are available for bond formation if the structure of the adsorbate molecule favours such bonding.

Chemisorption usually takes place at the surface sites associated with functional groups, like surface oxides, which constitute only a small portion of the total surface area but can still influence the characteristics of activated carbon substantially. The presence of surface carbonyl groups, for instance, enhances the adsorption of aromatic compounds, such as phenol, due to the formation of a donor-acceptor complex involving the benzene ring's π-electrons and the partial positive charge on the carbonyl groups. Carboxylic surface oxides, for example, would have a negative effect on the adsorption of phenol. They induce a polar character to the carbon surface, resulting in preferential adsorption of water molecules on these sites. These water-oxygen functional group complexes now prevent the migration of organic molecules to a large portion of the surface area.

1.2 Production and Activation

Activated carbon is produced from every conceivable form of carbonaceous material. The most common materials are wood, coal, peat, lignin, nut shell, sawdust, bone and petroleum coke. The nature of the starting material does not have a significant effect on the properties of the resulting activated carbon, since different characteristics can be induced by the selective introduction of additives and by controlling the production process.

The production of activated carbon involves a number of steps. Firstly, the raw material should be converted to a uniform particle size. By using techniques like high-pressure extrusion, pelletisation or agglomeration, one can influence the physical properties of the final product, such as granule size, particle size distribution, shape, roughness and hardness. Depending on whether the raw material contains carbohydrates or cellulose (e.g. wood), a second step, so-called carbonisation or pyrolysis, is introduced, whereby the raw material is slowly heated in the absence of air to temperatures below 600 °C to remove volatile pyrolysis products from the starting material. Finally the activation process takes place, during which the specific surface area of the carbon is increased by creating a microporous structure of tears, clefts and pores through a selective breakdown of the carbon.

One distinguishes between two different ways of activation. Firstly, chemical activation is used for non-charred (i.e. non-pyrolised) raw material such as sawdust and peat. These materials are treated with dehydrating additives like zinc chloride or phosphoric acid at high temperatures in order to obtain a wide-spread microporous system. Secondly, gas activation is used for charred raw materials like charcoal, peat coke and nut shell. By using either steam or CO_2 in a special furnace, like the most frequently used multiple hearth furnace at temperatures of about 800 to 1000 °C, the oxidising agents selectively attack portions of the char and transform it into gaseous products. The resulting hollow pores are systematically developed and enlarged.

Provided optimum activation conditions prevail, the loss of carbon during the activation process equals the increase in porosity. Thus the adsorption capacity can be measured gravimetrically by determining the bulk density.

1.3 Characterisation

The physical properties of activated carbon are mainly determined by the process of formation, the raw material, the method of activation and the parameters of activation, such as duration, temperature and type of furnace. By varying these parameters, one may obtain a suitable type of activated carbon for every application. The main physical characteristics by which activated carbon is judged, are outlined in the subparagraphs below.

1.3.1 Surface area and pore structure

Since the adsorption process mainly results in a concentration of solutes at the surface of activated carbon, one may expect the adsorption capacity to be proportional to the specific surface area. But the surface area alone is insufficient to explain the adsorption capacity of porous solids. It strongly depends on the pore size distribution, since micropores with a diameter of up to 20 Å constitute a major part of the specific surface area of activated carbon. The surface area accessible to the adsorbate depends on its molecular size, and only those pores which are accessible to the adsorbate will contribute to the effective or measured surface area. Thus activated carbon with a high specific surface area and micropores of a radius large enough for the desired adsorbates to fit in, is required [1].

One suitable method to determine the specific surface area was developed by Brunauer, Emmet and Teller (BET). The principle is to measure the number of nitrogen molecules adsorbed, provided that monomolecular adsorption takes place and that the space required by one nitrogen molecule is known. The surface area can then be determined by employing the BET equation [2, 6].

The preferred method to determine the pore size distribution is based on the so-called Kelvin equation. This equation relates the partial pressure of the adsorbate to the radius of those pores in which, on reaching a certain pressure, an equilibrium between condensation and evaporation of the adsorbate is attained [2].

1.3.2 Particle size and particle size distribution

Activated carbon is most commonly divided into granular activated carbon (GAC) and powdered activated carbon (PAC). Whereas GAC has an average particle size of a few millimetres, PAC particles are only a few micrometers large. The decision to use either GAC or PAC depends on the nature of the application. PAC is usually employed as a slurry in discontinuous processes, whereas GAC is used in fixed beds in continuous processes. An advantage of GAC over PAC in the case of water purification is the ease of handling and the simple separation of water and carbon on exhaustion [6].

The particle size distribution of GAC is best obtained by sieve analysis, whereas for the analysis of PAC a so-called coulter counter is a suitable device [7]. The results of the analysis are plotted in a RRS diagram, from which the average particle size and the homogeneity of the collected material can be obtained. Both parameters are essential to judge the fluid dynamical behaviour [5].

1.3.3 Density and hardness

For both density and hardness a number of measurement methods are available. Values of density and hardness should thus be specified along with the method used to obtain those values. A complete survey of such methods can be found in the literature [2, 6].

1.3.4 Design parameters

Especially for the treatment of surface water, manufacturers of GAC provide certain design parameters, like empty bed contact time, bed depth, linear velocity and backwash bed expansion, to assist in the design of adsorption columns and to simplify the optimisation of the adsorption process [8].

1.4 Existing Regeneration Methods

Once activated carbon is exhausted, i.e. the available surface is occupied by adsorbed components, it needs to be either discarded or regenerated. Due to the high manufacturing costs, on the one hand, and the recovery of components adsorbed on the surface, on the other hand, regeneration is the preferred option.

In fact, the possibility of regeneration is one of the main reasons for the widespread use of activated carbon as an adsorbent.

Regarding the regeneration of activated carbon one has to carefully distinguish between desorption and regeneration, on the one hand, and reactivation, on the other hand. Volatile components or substances adsorbed with lower energy can be removed fairly easily, whereas non-volatile compounds, substances adsorbed with high energy and so-called irreversible residues resulting from polycondensation or polymerisation product formation can hardly be desorbed. In this case reactivation of the activated carbon is essential to restore the initial adsorption capability [2].

The method of thermal regeneration combines both desorptive regeneration and reactivation as outlined above, whereas other existing regeneration methods, like extractive and chemical regeneration as discussed below, only utilises desorption to restore most of the initial adsorption capacity. However, in order to simplify matters, all methods will be referred to as regeneration methods [9].

1.4.1 Thermal regeneration

The thermal regeneration of activated carbon is usually carried out in the same devices used for the initial activation, like the multiple hearth furnace mentioned earlier. The three main parameters influencing the regeneration success are the temperature gradient within the furnace, the retention time and the level of exhaustion of the activated carbon.

A multiple hearth furnace consists of three main zones. In the first zone, the activated carbon is dried in a counterflow of combustion gases at about 100 °C. In the middle zone the regeneration takes place. At a temperature of about 400 °C in an oxygen-free atmosphere the volatile and slightly bound, mostly physisorbed components, are desorbed. In this zone the activated carbon surface is not modified yet. This happens in the last or reactivation zone, where the activated carbon is steamed at elevated temperatures of 870 to 980 °C. Substances still prevailing on the surface and also parts of the active surface itself become carbonised and subsequently gasified [10].

Even at these temperatures it is not possible to remove all contaminants from the surface. A further increase in temperature would lead to an unacceptable and expensive burn-out of the activated carbon. It causes an enlargement of the micropores, which constitute a major part of the adsorption capability. Thus, with an increasing number of thermal regeneration cycles, the adsorption capacity of the activated carbon decreases since the remaining components on the surface can neither be desorbed nor carbonised, and active carbon surface is lost through burn-out, as proven by a measured decrease in the BET surface area [9,11]. Further carbon loss (up to 10 mass percent of GAC) occurs as a result of attrition caused by the inevitable removal of the carbon from the column into the furnace. Another disadvantage of thermal regeneration is that the adsorbed compounds, which may be useful products like expensive solvents, are destroyed [11-12].

1.4.2 Extractive regeneration

Several process steps are involved in the extractive regeneration of activated carbon. In the first step, the adsorbed components are dissolved from the surface by using a suitable solvent. The solvent should meet certain requirements, including that the adsorbed components, as well as products formed by chemical reactions on the surface, should be soluble in the solvent, that the heat of solution should exceed the required heat of desorption, and that the solvent should be removable from the surface afterwards. In the second step the solvent and the dissolved components are separated by distillation. Finally, in the third step the carbon surface is relieved of the solvent by elevated temperatures and steam.

Although the activated carbon is in no way adversely affected by this regeneration method and an almost unlimited number of regeneration cycles is imaginable, the application of the technique is limited. This is attributed to the requirements the solvent has to meet, the large amount of solvent needed and the number of different process steps involved in carrying out one successful regeneration cycle [2].

1.4.3 Chemical regeneration

Chemical regeneration is based on the transformation of the adsorbed components into water soluble salts by adding diluted acids or bases. By employing this technique, it is possible, for instance, to desorb phenol from the surface of activated carbon by transforming it into water soluble sodium phenate with a sodium hydroxide solution.

Although this method is in no way harmful to the active carbon surface, the same restrictions as for extractive regeneration apply. Both the used chemicals and the desorbed substances need to be reprocessed in order to reduce chemical waste and financial expense. This limits the application to a few special cases [2].

1.5 A Potentially New State-of-the-Art Regeneration Method?

None of the three existing regeneration methods are capable of regenerating activated carbon to a satisfying extent. The thermal method is widely applied to all types of pollutants/carbons, but due to the high temperature needed it is very energy consuming and harmful to the surface as a result of the internal burn-out of the micropores. Neither the extractive nor the chemical method affects the surface in any way, but these methods are only viable when adsorbates are lightly bound to the surface and can thus be easily desorbed. Moreover, the requirements for solvent removal from adsorbents and for exhausted solvent recycling should be met [13].

Supercritical fluid extraction (SFE) has in recent years been proven successful for a variety of laboratory scale experiments. It features many of the advantages of the existing methods and simultaneously excludes a few of their disadvantages. Many of the investigations performed on loaded activated carbon samples showed promising results similar to those obtained in preliminary investigations [3, 13-17].

2. BASICS OF EXTRACTION

The basic principle of all methods of separation, of which extraction is an example, is to divide a mixture of components, either by employing an auxiliary agent (like a solvent) or by adding energy (like in distillation), into at least two different products.

2.1 Conventional Extraction

For extraction suitable solvents are used to either recover a valuable product from a solid matrix or to dissolve pollutants from raw material and thus purify the material itself. After extraction, one is left with the leached matrix and the extract, which contains the solvent and the dissolved components [18]. In a second step the solvent itself should be separated from the dissolved components to yield pure solvent for the next extraction and to recover potentially valuable products. This step, usually carried out as a distillation, is often expensive and poses high demands onto the solvent in addition to the normal requirements the solvent should meet in order to enable a successful and safe extraction:

- high selectivity
- high capacity
- neither poisonous nor flammable or environmental harmful
- inert chemical and physical behaviour
- low boiling point and low specific heat capacity (easy regeneration by distillation)
- low viscosity (low mass transfer resistance)
- inexpensive and readily available

Due to the large number of requirements and the possible conflicts among these (selectivity normally excludes high capacity, highly selective and high-capacity solvents usually are neither inexpensive nor readily available), it is often difficult to identify a suitable solvent for a given extraction [5].

The solid matrix designated for extraction is usually characterised by a marked pore structure, which causes a large part of the extraction to take place at an internal surface. Thus a number of single steps, as shown in figure 1, are required to obtain successful mass transfer from the pores into the free liquid.

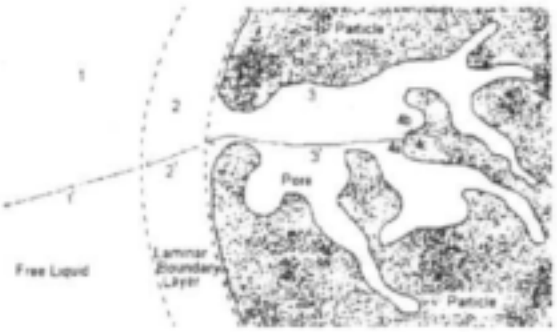

Figure 1: Single Pore Model [5]

At first, the solvent is transported to the particle by convection (1). The laminar boundary layer surrounding the particle is surmounted by film diffusion (2), and as soon as the solvent has reached a pore, the transport mechanism changes to pore diffusion (3). In the pore, dissolution (4a) and/or desorption (4b) take place, or prior to both, a diffusive transport of components through the solid material to the pore surface (4c). The loaded solvent reaches the free liquid again, firstly by pore diffusion (3') and secondly by film diffusion (2') and is finally removed by convection (1').

In principle, each of the four steps involved in extraction can limit the process, but since both convection and film diffusion can be altered simply by increasing the flow velocity, the steps considered to limit the extraction usually are pore diffusion and dissolution. The influence of these parameters is shown in figure 2 by virtue of a yield of extraction vs. extraction time curve.

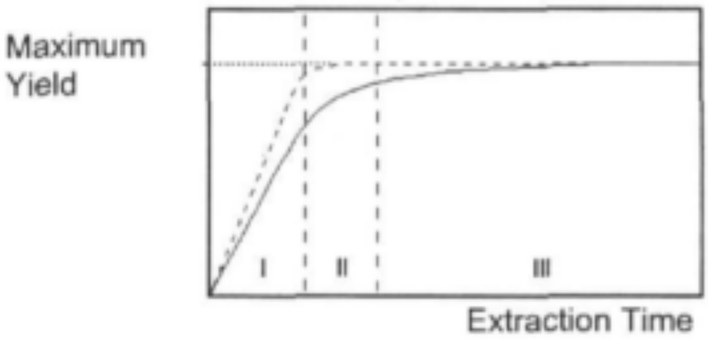

Figure 2: Kinetic Curve [18]

The graph can be divided into three time zones. In zone (I), at the beginning of the extraction, the solvent washes out the desired components from the easily accessible pores. The gradient of the curve is constant, which indicates that the extraction at this stage is only limited by the dissolution capacity of the solvent. In zone (II), known as the transition region and indicated by a bend in the curve, the easily accessible pores are almost washed out and the influence of pore diffusion begins to dominate the extraction. In zone (III) the pore diffusion completely limits the process, which manifests itself by a maximum in the curve towards the end of the extraction.

The effect of pore diffusion can be reduced by reducing the particle size as shown by a dominantly horizontal progression of the graph after the initial constant gradient, and the dissolution step can be optimised by employing a suitable solvent and the right conditions as shown by an increase in the initial gradient of the curve at the beginning of the extraction. The dotted line in figure 2 gives the kinetic curve for such an optimised process, which provides the same maximum yield but within a shorter extraction time [18].

2.2 Supercritical Fluid Extraction

SFE is a process utilising gases under supercritical conditions as solvents to extract desired substances from given matrices. For transforming a gas or a liquid into a supercritical fluid, it is essential to exceed the critical pressure p_C and the critical temperature T_C indicated as the critical point CP in the equilibrium phase diagram in figure 3. Once the supercritical region is reached, it is no longer possible to distinguish between a gas or a liquid, since only one phase exists beyond the termination of the vapour curve at the critical point [19].

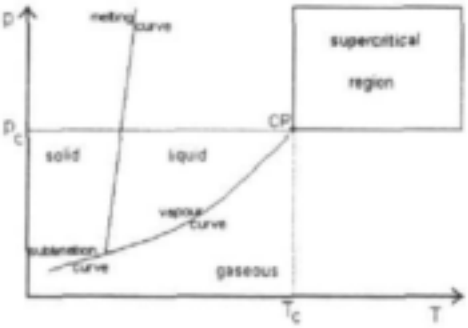

Figure 3: Equilibrium Phase Diagram [20]

Table 1 gives the critical constants for some selected gases used in SFE.

Table 1: Critical Constants [18]

Gas	Critical Temperature [ºC]	Critical Pressure [bar]
Carbon Dioxide	31.0	72.9
Ethane	32.2	48.2
Propane	96.8	42.4
Toluol	321	41.6

The fluids exhibit both the properties of the corresponding gases and liquids. The viscosity and diffusion coefficients are comparable to those of gases, whereas the densities are similar to those of liquids [19]. Table 2 shows the range of these parameters for gases, liquids and supercritical fluids.

Table 2: Physical Properties [18]

	Density [g/cm^3]	Viscosity [g/cm·s]	Diffusion Coefficient [cm^2/s]
Gas	$(0.6\text{-}2)\cdot 10^{-3}$	$(1\text{-}3)\cdot 10^{-4}$	0.1-0.4
Liquid	0.6-1.6	$(0.2\text{-}3)\cdot 10^{-2}$	$(0.2\text{-}2)\cdot 10^{-5}$
Supercritical Fluid	0.2-0.9	$(1\text{-}9)\cdot 10^{-4}$	$(0.2\text{-}0.7)\cdot 10^{-3}$

The liquid-like high density is responsible for the high solubility of substances in supercritical fluids. It is influenced by both the temperature and the pressure. With increasing pressure the density increases, and with increasing temperature the density decreases, and the solubility varies correspondingly.

Since temperature does not only affect density but also the vapour pressure of the components to be dissolved in the supercritical fluid, an increase in vapour pressure resulting from a rise in temperature may cause an increase in solubility. This effect can cancel out or even reverse the normally expected decrease in solubility due to decreasing supercritical fluid density with rising temperature [21-22]. Both effects (low density vs. high vapour pressure) come into play only at rather high temperatures, which may be necessary for the desorption and/or dissolution of components from the surface of a solid matrix.

The gas-like viscosity enables the supercritical fluid to easily diffuse through pores and to transport the dissolved components faster than liquids. The resulting low mass transfer resistance is also obvious from the diffusion coefficients.

Finally, the separation of the dissolved components and the supercritical fluid does not require energy like in conventional extraction. By adjusting conditions to below the critical temperature and pressure, the density instantaneously decreases to the extent of a normal gas and the dissolved components fall out of the gas. This results in a very simple regeneration of the solvent in the case of SFE.

The preferred solvent meeting the requirements mentioned above (neither poisonous nor flammable or environmentally harmful, inert chemical and physical behaviour, cheap and readily available) is CO_2. It has rather moderate values for critical temperature and pressure as shown in table 1, allowing extractions to be performed at temperatures as low as 35 °C.

A last criterion for solvents, namely selectivity, is determined by the structure of the CO_2 molecule. According to a difference of 1.0 in electronegativity between oxygen and carbon, one would expect CO_2 to behave hydrophilic, but due to the linear structure of the molecule it exhibits a rather hydrophobic character [23]. The selectivity thus favours the extraction of hydrophobic components, and in order to extract hydrophilic components, one needs to add to the *sc*-CO_2 small amounts of modifier, like methanol, ethanol or acetone, which enable hydrophilic components to dissolve in *sc*-CO_2.

3. SELECTION OF SUITABLE WATER PURIFICATION INSTALLATIONS

3.1 Use of GAC in Water Purification Plants

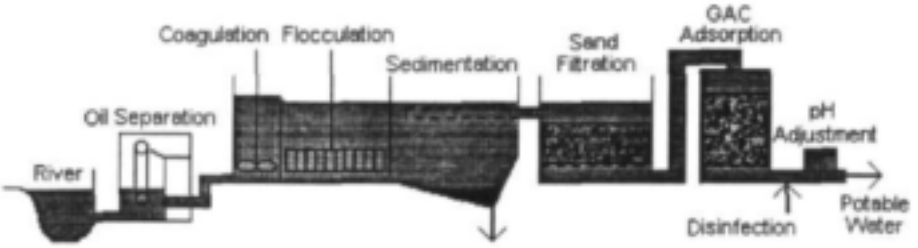

Figure 4: Flow Sheet for Water Purification Plant [24]

A flow sheet showing a general water purification plant is presented in figure 4. Water from a river is systematically taken through a number of purification processes to a stage where it is distributed for human consumption. In a first step, oil is separated from the water using a belt skimmer. Following this step, coagulation and flocculation are carried out by adding hydrated lime and activated silica to precipitate the dissolved and the suspended solids as macromolecules. These are separated from the water in the sedimentation step. Any small molecules and solid particles which do not settle fast enough are removed in the sand filtration step. In the next step, the TOC (Total Organic Carbon) is removed by adsorption onto a fixed bed of GAC, where TOC includes organic contaminants, pesticides, micropollutants, humic acids and detergents, usually in very low concentration. After this, a disinfection is performed by adding chlorine in order to decompose bacteria. Finally, the pH is adjusted from 11.5 (caused by the hydrated lime) to 8.5. The potable water is then pumped into the municipal water network. [8, 24]. The GAC adsorption is not necessarily performed in a separate column. It is also possible to add GAC to the sand filter bed and combine the removal of small solid compounds and of TOC in a single step. Each water purification installation follows its own operational procedure to purify water, as will be explained later in more detail for the installations from which samples of GAC were collected for investigation.

3.2 Location of Selected Sites in Southern Africa

Three installations at quite different locations spread all over southern Africa as shown in figure 5 were selected. The selection was based, on the one hand, on the different raw water qualities in these areas as a result of different sources of origin and, on the other hand, on the similar types of GAC used in order to exclude type of GAC as another variable influencing the regeneration. The three selected types of water would presumably contain different contaminants to be adsorbed on the GAC, and this could affect the regeneration success. The best way to detect such differences in contamination and regeneration would be to have a similar type of GAC throughout.

Figure 5: Location of Selected Water Purification Plants in Southern Africa

The selected water purification installations are briefly summarized below.

1. In the case of the Zuikerbosch Pumping Station managed by Rand Water in **Vereeniging**, surface water from the Vaaldam is purified, and at Barrage Water Purification Installation, also run by Rand Water, potable water is produced from river water contaminated by industrial run-off and polluted inflows.

2. At the Umgeni Water Process Evaluation Facility situated at the Wiggins Water Works in **Durban** bad odour and taste need to be removed from the surface water of the Inanda Dam in the Umgeni River.

3. At the Goreangab Reclamation Plant in **Windhoek**, Namibia, fresh water containing domestic sewage water, stormwater run-off and small amounts of industrial waste water is purified.

3.3 Description of Selected Water Purification Systems

3.3.1 Rand Water Vereeniging

Zuikerbosch Pumping Station: A volume 2 200 megaliters of water is purified daily. The pH adjustment is situated between the sedimentation and the sand filtration. Another deviation from the general purification plant shown in figure 4 is the lack of a GAC adsorption facility, but the potential advantage of such a facility is investigated separately in a pilot plant purifying daily 7 megaliters of sand filter backwash water containing a high amount of TOC. The F400 GAC samples taken from this pilot plant were exhausted for barely 100 h and had never been regenerated before. A virgin F400 sample was also collected.

Barrage Water Purification Installation: The installation works on a pilot plant scale, provides potable water for about 400 people and conforms to the plant presented in figure 4. Samples of both regenerated and exhausted GAC were collected. The exhausted sample stayed in the column for about one year and had been thermally regenerated before.

3.3.2 Umgeni Water Durban

Umgeni Water Process Evaluation Facility: In the main plant 350 megaliters of water is purified daily. The plant involves a pre-ozonation step, but no GAC adsorption and pH adjustment. The effect of GAC adsorption on the improvement of the water quality is investigated in a pilot plant just like at the Zuikerbosch installation above. A volume 2.5 kiloliters of water is treated per hour in this plant by coagulation, flocculation, sand filtration and GAC adsorption. It takes about 18 months to exhaust the GAC, and samples of such exhausted but not previously regenerated carbon were chosen for investigation. These samples included carbons of the type F400, Diahope 006 and Picabiol.

3.3.3 Windhoek City Council

Goreangab Reclamation Plant: The purification plant is similar to the one explained in figure 4, except that the flocculation and sedimentation steps are replaced by air flotation. This installation is the only one of the three investigated plants using GAC to remove TOC from the water on an industrial scale. A volume 7.2 megaliters of water is purified daily. The GAC is usually exhausted after 6 months and then regenerated thermally. The columns are refilled with a mixture of virgin and repeatedly thermally regenerated GAC. Samples of such a mixture of virgin and regenerated and a true virgin F300 GAC were obtained for investigation.

3.4 Characterization of GAC Samples

From the installations listed GAC samples of the types F300, F400, Diahope 006 and Picabiol were investigated. Their properties were characterized according to the procedures outlined previously, and the results are presented in table 3. Picabiol GAC, a wood-based carbon exhibiting a macroporous structure with a specific surface area of 1500 m^2/g was only investigated to marginally test the feasibility of SFE regeneration with a GAC having biological rather than adsorptive properties. Once the carbon has been exposed to the water for some time, a biological layer covering the outer surface of the activated carbon develops. The biodegradable organic compounds in the water do not adsorb on the inner surface area of the GAC, but are broken down by the biological layer. Only the remaining non-biodegradable micropollutants, such as pesticides, are commonly adsorbed.

Depending on the amount of non-biodegradable micropollutants available for adsorption, regeneration of the carbon may not be necessary at all.

Table 3: GAC Properties [8], [25]

	F300	F400	Diahope 006
Raw material	Bituminous coal	Bituminous coal	coal
Specific surface area [m^2/g]	1000	1100	1150
Pore structure	Microporous	Tridisperse	Microporous
Mean particle diameter [mm]	1.6	1.0	1.0
Particle size distribution [mm]	0.6-2.36	0.425-1.7	0.425-1.7
Superficial velocity [m^3/m^2h]	5-20	5-20	5-20
Bed density [g/ml]	0.46	0.425	0.48
Hardness [%]	75	75	94
Bed depth [mm]	750	750	900
Pressure drop [mbar/m bed depth]	10-40	15-80	5-30

4. EXPERIMENTAL AND TECHNICAL DETAILS

4.1 Bench-Top Supercritical Fluid Extractor

The instrument utilised to perform supercritical extractions is a Varian Star SFE PrepMaster (II), linked to a Varian Star SFE Accutrap (III) and a Varian Star SFE Modifier Pump (I), as shown in figure 6. A flow-sheet depicting its operation is presented in figure 7.

Figure 6: Supercritical Fluid Extractor [3]

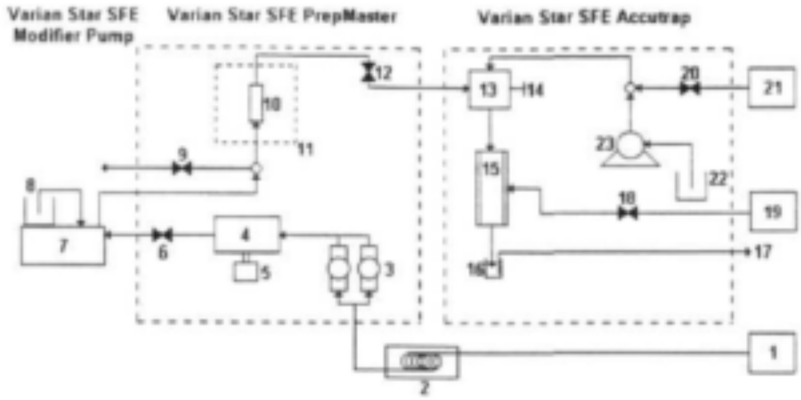

Figure 7: Flow Sheet for Supercritical Fluid Extractor [26]

The highly-pure SFE grade CO_2 (99.99%) is stored in a conventional gas cylinder (1), pressurised with helium to maintain a bottle pressure between 100 and 130 bar as required for the withdrawal of liquid CO_2 for the entire contents of the cylinder. Since small amounts of CO_2 may evaporate in the flow line, the liquid gas passes a water cooler (2) to ensure that only pure liquid gas is supplied to the extractor.

The gas enters the dual piston pump (3) with which pressures between 130 and 450 bar can be obtained. After passing the dampening chamber (4) with its safety head (5) and the manual on/off valve (6), it enters the modifier pump (7). If desired, an amount between 0.1 and 99.9 vol % of modifier (8) may be added to the *sc*-CO_2. If the vent/purge valve (9) is closed, the gas finally enters the extraction vessel (10) installed in a temperature-controlled oven (11). Here a temperature of up to 150 °C can be obtained by electrical heating. The supercritical gas and dissolved extract leave the extractor through switching valve (12) and enter the accutrap. Depending on the valve position (open or close), the extraction takes place statically or dynamically.

In the restrictor (13) atmospheric conditions are restored. The temperature is adjusted between 20 and 100 °C by electrical heating to compensate for the Joule-Thomson effect. The flow rate through the restrictor is controlled with an automatic valve (14) in a range between 1 and 7 ml/min.

The substances dissolved in the *sc*-CO_2 drop out in the restrictor (13) and are collected in the trap (15) by adsorption on small glass beads. The gas exiting from the trap (15) and passing through the collection vial (16) is finally released into the atmosphere (17) to complete an open loop process.

The trap (15) can be cooled down to –50 °C by opening valve (18) to enable compressed CO_2 from a gas cylinder (19) to expand in the trap (15). This is useful for keeping highly volatile extraction products in the trap. When an extraction is finished, valve (12) is closed and the extracted substances are flushed out of the trap (15) into the collection vial (16) either by opening valve (20) to use N_2 or by pumping a suitable solvent (22) through the trap by a solvent pump (23). This flushing process can be supported by heating the trap and thus desorbing the components from the glass beads and ensuring their dissolution in the flushing solvent.

Operating the instrument is fairly simple. The extraction vessel with either 3 or 5 ml capacity contains the GAC to be extracted and is closed on both ends with porous seals avoiding solid material to contaminate the flow line, and screwed together with end-caps as shown in figure 8.

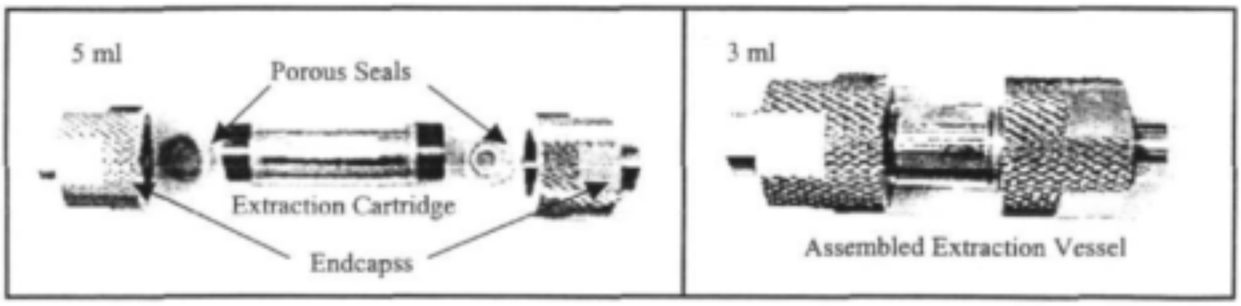

Figure 8: Extraction Vessel [3]

Except for the vent/purge and the on/off valves, all other valves as well as the oven, restrictor and trap temperature, the flow rate of the modifier pump, the solvent and main pump and the system pressure are automatically controlled by the built-in microprocessor and software. Both set and actual values are permanently displayed during the extraction process.

4.2 Method of Analysis

A substance which is easily adsorbed onto activated carbon is iodine, and the milligrams of iodine adsorbed by 1 g of carbon from aqueous iodine solutions, called the iodine number, gives fairly accurate information on the available free surface area of a given GAC sample. The advantage of the method is that only basic laboratory hardware is needed to conduct the determination. Moreover, if the equilibrium concentration of the iodine solution after adsorption is 0.02 N, one may assume that the iodine is adsorbed onto the activated carbon as a monomolecular layer like nitrogen in BET determinations. Then there is a correlation between the BET surface area and the iodine number as shown in figure 9 [2].

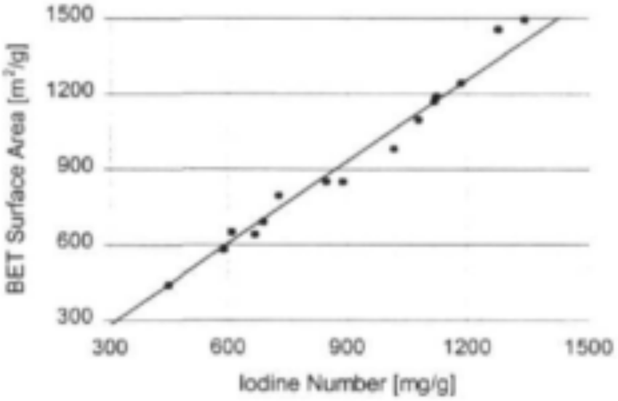

Figure 9: BET Surface Area vs. Iodine Number [2]

The linear regression line indicates that up to a surface area of approximately 1200 m^2/g a linear relation exists between the surface area and the iodine number. The iodine number is thus sufficient to determine the specific surface area of activated carbon having a total virgin surface area not exceeding 1200 m^2/g.

A sample of GAC is ground until at least 95 mass percent meets the requirement of a particle size of 44 μm or less. The sample is dried for at least 2 hours at (110 ± 5) °C, cooled to room temperature and boiled with hydrochloric acid solution to remove any sulphur that could interfere with the test results. A known volume of standard iodine solution is added to this mixture, filtered afterwards and the filtrate titrated with standard sodium thiosulfate solution and starch solution as an indicator in order to determine the molar concentration of the residual iodine solution. This concentration should ideally be as close as possible to 0.02 N or should at least be in the range 0.008 to 0.04 N.

The procedure is repeated until a mass is identified that causes the residual iodine concentration to fall within the required range. A real iodine number determination can then be performed. For this, three slightly different sample masses are calculated based on the iodine number estimated by the preliminary runs, and three determinations are performed such that none of the three residual iodine concentrations falls outside the range. From these concentrations the milligram iodine adsorbed per gram of activated carbon is calculated and plotted on a log-log diagram versus the corresponding concentrations. Figure 10 gives an example of such a diagram.

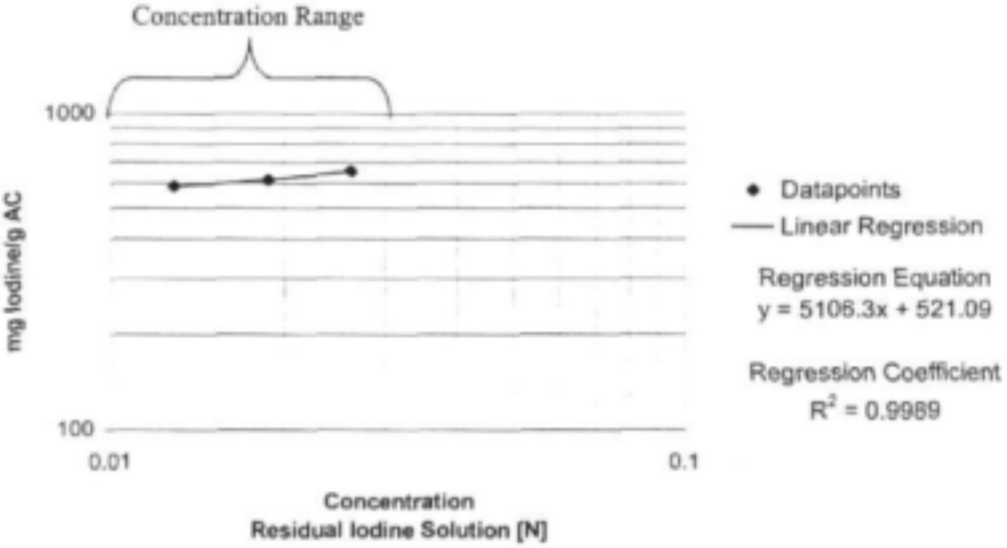

Figure 10: Log-log Diagram

The three values are interpolated by a linear regression line, and if the regression coefficient R^2 is larger than 0.995, the real iodine number adequately representing the BET surface area is calculated from the equation describing the regression line and a normality of 0.02 N as the x-value. If either the regression coefficient or one of the residual concentrations does not meet the set requirements, the determination needs to be repeated.

Another, much faster possibility to determine the iodine number, is to perform a single run. The normality of the residual iodine solution must also fit into the required range, and the milligram iodine adsorbed per gram of activated carbon is calculated again from this concentration. If the normality of the residual iodine solution does not equal 0.02 N, correction factors are used to adjust the result for the proper iodine number [27]. However, the first method was preferred, since in the preliminary tests its accuracy had proved to be higher.

4.3 Statistical Design

Pressure and temperature were found to be the main parameters influencing the regeneration process and the resulting iodine number. Due to the tedious procedure to determine the iodine number, it was important to extract the maximum amount of unbiased information regarding the effect of pressure and temperature on the iodine number from as few experiments as possible. In order to achieve this goal, a statistical composite surface design available in the computer software package "Statistica for Windows CSS" [28] was employed.

In principle, the program requires a certain number of temperature/pressure parameter pairs, called a design, to be performed. For each run the iodine number is determined and these observed values are fitted by the software as a function of the independent variables (temperature and pressure) according to a mathematical model. Based upon this model, a surface response graph is calculated. It represents the dependence of the iodine number (dependent variable) on pressure and temperature (independent variables) for one specific GAC sample.

A rotatable, and orthogonal or nearly orthogonal design can be obtained by adding so-called star points to a simple 2-by-2 orthogonal design matrix as shown in table 4. The first four runs represent a 2-by-2 orthogonal design, runs 5 to 8 are the so-called star points, and runs 9 and 10 are centre points. The information function for this second-order or quadratic design is rotatable, i.e. constant on circles around the origin. The rotatability of the design refers to the characteristic that it can yield the same amount of information (i.e. make predictions to the same extent of precision) in all directions of the fitted surface. A design is orthogonal if all estimates in the second-order model are uncorrelated. [28-32].

Table 4: Rotatable Design

	Independent Variable I	Independent Variable II
Run 1	1	1
Run 2	1	-1
Run 3	-1	1
Run 4	-1	-1
Run 5	-1.414	0
Run 6	1.414	0
Run 7	0	-1.414
Run 8	0	1.414
Run 9	0	0
Run 10	0	0

The accuracy of the mathematical model, referring to the extent to which the calculated values correspond with the measured values, can be gathered from a graph showing the predicted (model) vs. the observed (experiment) values. The better the data points fit on a straight line, the more reliable the model is.

With the strategy outlined above, it was possible to determine the influence of both pressure and temperature on the regeneration within the experimental region by only ten runs. The pressure and temperature values in table 5 were calculated by the program according to the design in table 4 within the ranges concerned.

Table 5: Experimental Design

Run	Pressure [bar]	Temperature [°C]
1	375	130
2	375	50
3	135	130
4	135	50
5	90	90
6	430	90
7	260	33
8	260	146
9	260	90
10	260	90

4.4 Experimental Procedure

A GAC sample with a mass sufficiently large to properly fill the 5 ml extraction vessel (about 2,5 g to 3.0 g) is placed into the extraction vessel and sealed off as illustrated in figure 8. The tightly closed vessel is connected into the flow line shown in figure 7 by screwing slip-free connectors into the endcaps of the vessel. Then the extraction and collection methods are programmed, and after closing the vent/purge valve (18), opening the on/off valve (6) and opening the valves of the gas supply cylinders (1, 19, 21), the extraction process is started. Until all actual values meet the set values, the automatic switching valve (12) stays closed. As soon as equilibrium is accomplished, valve (12) opens and the extractor starts to control the flow rate of the *sc*-CO_2 and the modifier (if applicable) to meet the set values. As soon as the extraction time expires, the gas flow is interrupted by an automatic closure of valve (12), and the substances collected in the trap are flushed into 2 ml vials by employing either methanol or acetone as solvent. The flushing is performed in triplicate. The contents of the first vial can be used for analysis, if desired, whereas the two subsequent flushings only serve to purge the trap. The contents of these vials are, therefore, usually rejected.

After the flushing step, the extraction cycle is complete. The vials are replaced by empty ones, and pressure is released from the system, except for the dampening chamber (4) and the pump (3), by first closing the on/off valve (6) and then opening the vent/purge valve (9). The extraction vessel is removed once the automatic cooling system has decreased the oven temperature to 30 °C. The vessel is opened, the GAC sample is poured into a sample vial and its mass is determined on a precision balance once all CO_2 has left the pores and no mass changes occur. For the determination of the mass loss the moisture contents of the samples does not need to be considered, since the samples are fully dried before the extraction and stored under atmospheric conditions to equalise the moisture contents caused by air humidity before and after extraction.

The vessel can be filled again, and after the new extraction parameters are set, the next extraction run can be performed. After the last run, the valves of the supplying gas cylinders (1, 19, 21) are closed, and the whole system is relaxed by opening both the on/off valve (6) and the vent/purge valve (9).

After monitoring the mass loss, the samples are ground for 10 minutes in a ball mill. The duration of grinding was set to acquire a particle size of maximally 44 µm. After grinding, the samples are dried for at least 2 hours, cooled down to room temperature in a desiccator afterwards, and then subjected to iodine number determination.

For the analysis, three samples with slightly different mass (between 0.6 g and 1.0 g) are put into 250 ml flasks with ground glass stoppers. Into these, 5 ml of the hydrochloric acid solution are pipetted, the flasks are closed and swirled gently, and the contents is boiled for 30 seconds on a hot plate. After cooling to room temperature, 50 ml of standard iodine solution is added into each flask, the flasks are closed again and shaken vigorously for 30 seconds before the contents is filtered. An aliquot of 25 ml of the filtrate is titrated with standard sodium thiosulfate solution, and from the volume used, the concentration of the residual iodine solution and the milligram iodine adsorbed per gram of activated carbon are calculated. The three data points are plotted on a log-log diagram, and from this the iodine number is calculated.

5. RESULTS FOR REAL-WORLD GAC REGENERATION

5.1 Process Optimization

5.1.1 Precision Control of iodine number determination

Table 6: Iodine Number Test Results

Determination	Iodine Number
1	1087
2	1080
3	1074
4	1079
5	1086
6	1070
7	1075
8	1079
9	1075
10	1081

A virgin GAC F400 sample was selected for 10 successive determinations of the iodine number under identical conditions to determine the precision of the analytical method. The corresponding values are listed in table 6. The average iodine number [33] turned out to be 1079 ± 5, which is in fair agreement with that specified by the manufacturer [8], rendering the iodine number determination a precise tool to monitor the regeneration process and to judge its success, provided that the determinations are all performed in exactly the same way. This requirement was indeed met for the determinations in this investigation.

5.1.2 Statistical surface response analysis

An extraction time of 90 minutes was selected for the 10 runs envisaged according to the statistical design discussed earlier and the results for the Umgeni samples as a representative example are summarised in table 7.

Table 7: Results of Experimental Design Runs for Umgeni Samples

Run	Pressure [bar]	Temp. [°C]	Flow Rate [ml/min]	Time [min]	Density [g/ml]	Iodine Number
1	375	130	2	90	0.64	802
2	375	50	2	90	0.91	778
3	135	130	2	90	0.23	776
4	135	50	2	90	0.66	779
5	90	90	2	90	0.17	770
6	430	90	2	90	0.81	785
7	260	33	2	90	0.91	784
8	260	146	2	90	0.44	806
9	260	90	2	90	0.65	789
10	260	90	2	90	0.65	785

With the 10 iodine numbers a surface response graph was calculated. It is shown in figure 11. The reliability of the mathematical model employed to calculate the surface response graph is proven by figure 12, showing that the predicted versus observed values for the 10 pressure/temperature parameter pairs fit closely onto a straight line. The surface response graph thus describes the relationship among iodine number, pressure and temperature within the experimental range quite well.

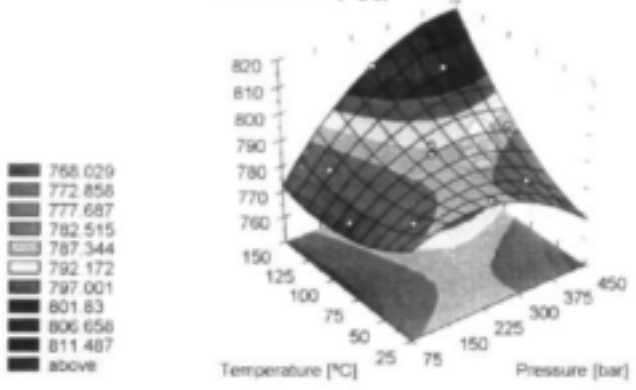

Figure 11: Surface Response Graph

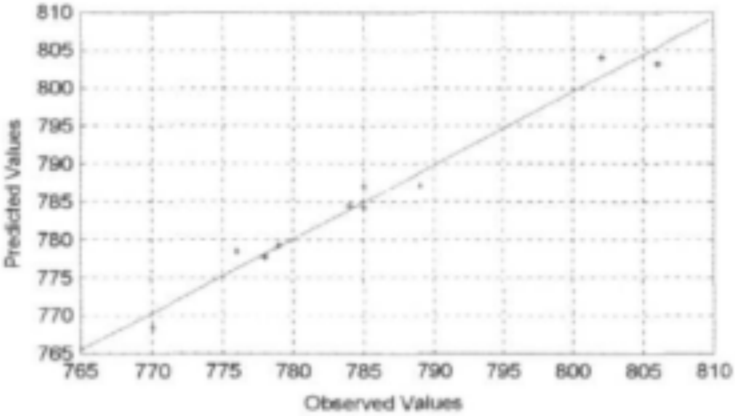

Figure 12: Accuracy of the Model

One may conclude from the surface response graph that the optimum conditions for regeneration within the operational range of the supercritical fluid extractor are 150 °C and 450 bar. The corresponding density under these conditions is 0.65 g/ml, which is a moderate number suggesting that desorption rather than dissolution is mainly responsible for the removal of contaminants from the carbon surface.

5.2 Supercritical Fluid Regeneration Results for Selected Sites

5.2.1 Umgeni Water

The maximum iodine number of 815 obtained on regeneration is only slightly higher (~ 7.5 %) than the iodine number of 758 of the exhausted sample, showing that it was not possible to regenerate the activated carbon samples significantly by SFE. The regeneration results are somewhat better for the F400 than for the Diahope 006 sample (from natural raw water) as shown in figure 13, though both were exposed to exactly the same raw water under the same conditions over the same period of time (18 months). This shows that both types of carbon, although having similar physical properties, exhibit different adsorption behaviour.

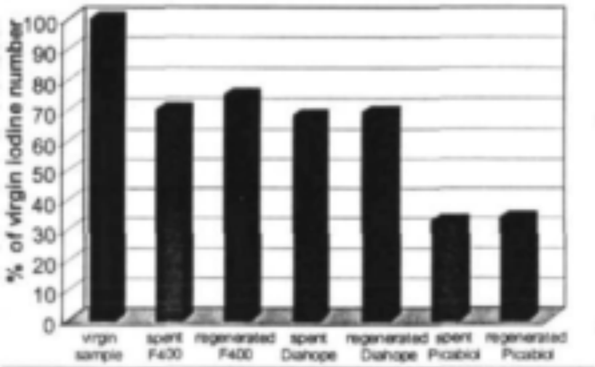

Figure 13: Iodine Number Comparison for Umgeni Samples

The wood-based Picabiol GAC was only investigated to check the feasibility of regeneration by SFE. Only one run was performed under the same optimum conditions as those applied to the F400 and Diahope 006 samples. The virgin iodine number is higher, and the iodine number of the exhausted sample much lower than those of the other two GAC samples (F400, Diahope 006). From the iodine number of the regenerated sample it is clear that it was impossible to regenerate the Picabiol sample at all. The reason probably is that the wood-based carbon does not primarily adsorb organic substances, but rather breaks these down by growing a biological layer on its surface which cannot be destroyed by any of the known regeneration methods.

5.2.2 Rand Water

The F400 sample from the Zuikerbosch pumping station was exposed over a very short period of time (100 hours) as mentioned previously. Consequently, the iodine number decreased from 1079 for the virgin sample to only 944 for the exhausted sample.

Though employed to purify a different type of raw water than at Umgeni Water, the same type of GAC (F400) is used at Zuikerbosch. Therefore, the same 10 regeneration runs (paragraph 5.1.2) were performed to establish the influence of temperature and pressure on the regeneration. The results are summarised in table 8.

Table 8: Results of Experimental Design Runs for Zuikerbosch Sample

Run	**Pressure [bar]**	**Temp. [°C]**	**Flow Rate [ml/min]**	**Time [min]**	**Density [g/ml]**	**Iodine Number**
1	375	130	2	10	0.64	946
2	375	50	2	10	0.91	946
3	135	130	2	10	0.23	953
4	135	50	2	10	0.66	947
5	90	90	2	10	0.17	952
6	430	90	2	10	0.81	946
7	260	33	2	10	0.91	938
8	*260*	*146*	2	*10*	*0.44*	*997*
9	260	90	2	10	0.65	942
10	260	90	2	10	0.65	941

The regeneration under the various conditions yielded iodine numbers ranging from 938 to 997. Compared to the iodine number of 944 for the exhausted sample, and bearing in mind the precision of the iodine number determination of about ± 1.5 %, it follows that in the majority of cases the iodine number was either left unchanged or only slightly improved by the regeneration attempts. However, at least in one case (run 8) a recovery of the initial adsorption capacity to 92.5% was accomplished. This was achieved at the same conditions that proved to be optimum for the regeneration of the F400 sample of Umgeni Water. The only difference is that the Zuikerbosch F400 sample was only regenerated for 10 minutes, since an extended regeneration of 90 minutes did not result in any improvement. This suggests that for both F400 samples, regardless of the type of raw water, the same mechanism of regeneration applies.

To save on the expense of virgin activated carbon, mixtures of unused and previously regenerated GAC are employed as "virgin" activated carbon at Barrage Water Purification Installation. The "virgin" mixture thus has quite a low iodine number of 603. For the spent sample, which was exhausted in a column for about one year, the iodine number is 582. The extremely small difference shows that almost no contaminants in the water are adsorbed on the GAC, and that probably only TOC is removed by the limited adsorption capacity of the mixture.

Since both the virgin and exhausted samples consist of spent GAC, both were subjected to supercritical fluid regeneration. The same regeneration parameters used for the F400 sample from Umgeni Water yielded iodine numbers of 665 for the virgin and 641 for the exhausted sample, respectively. In both cases the regeneration resulted in an increase of 10% in the iodine number. Due to a lack of information on the physical properties of this GAC (type of raw material, real virgin iodine number) an evaluation of the 10% increase in iodine number in both cases as a good or bad result is not possible. Nevertheless, the parameters favouring desorption once again prove to have yielded the best results.

5.2.3 Windhoek City Council

The iodine number of 597 for the exhausted sample shows that the GAC used at Windhoek City Council's Goreangab Reclamation Plant got fairly exhausted during a short exposure period of 6 months. A few preliminary runs were performed with an extraction time of 90 minutes, but the iodine numbers could hardly be improved. However, in contrast to all other samples investigated, a remarkable mass loss of more than 20% was observed. Hence, the 10 usual runs based on the statistical experimental design (paragraph 5.1.2) were performed with an extraction time of 10 minutes and monitored in terms of mass loss rather than iodine number. The results are summarised in table 9. With these results, a surface response graph was calculated with mass loss instead of iodine number versus temperature and pressure. A straight line proved the reliability of the model developed to calculate the surface response graph and thus allowed prediction of mass loss over the whole measurement range with accuracy.

Table 9: Results of Experimental Design Runs for Windhoek Samples

Run	**Pressure [bar]**	**Temp. [°C]**	**Flow Rate [ml/min]**	**Time [min]**	**Density [g/ml]**	**Mass Loss [%]**
1	375	130	2	10	0.64	2.2
2	375	50	2	10	0.91	1.2
3	135	130	2	10	0.23	1.1
4	135	50	2	10	0.66	0.5
5	90	90	2	10	0.17	0.3
6	430	90	2	10	0.81	1.6
7	260	33	2	10	0.91	0.9
8	260	146	2	10	0.44	2.3
9	260	90	2	10	0.65	0.6
10	260	90	2	10	0.65	0.8

In order to explain the results, a mass loss versus time curve as shown in figure 14 was determined. Although, according to the surface response graph in figure 11, extreme conditions (450 bar, 150 °C) were found to be the optimum parameters, more moderate conditions (375 bar, 130 °C) were chosen to perform these measurements. This was done since, on the one hand, time could be saved by more promptly establishing equilibrium conditions at moderate than at extreme conditions and, on the other hand, the same information could be retrieved from results obtained at milder conditions.

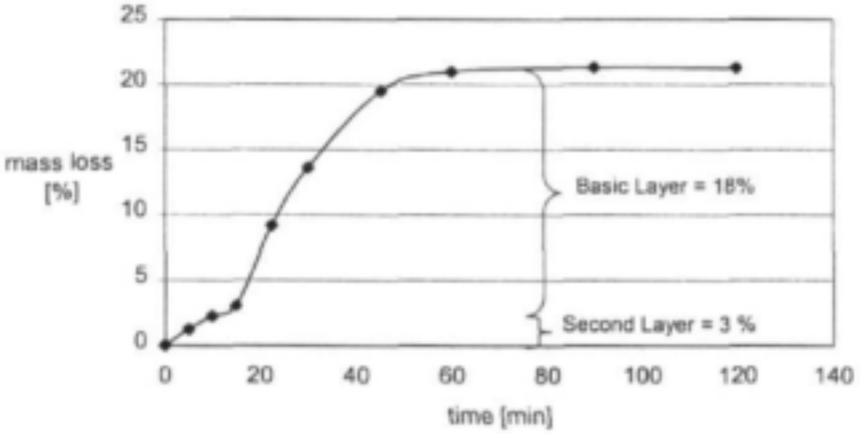

Figure 14: Mass Loss vs. Time Curve

The resulting curve exhibits a two-layer desorption process completed after 60 minutes. The first three mass percent was not removed directly from the surface but from a layer adsorbed on the surface. Once the secondary layer had been removed, the primary layer could be desorbed to make free surface area available. The F300 sample from Goreangab Reclamation Plant consists of a mixture of virgin and repeatedly thermally regenerated exhausted GAC. The mass loss is believed to result from the regenerated portion of the mixture. Yet, the iodine number reflects free surface area associated with the virgin portion. On removing the secondary layer, some contaminants may be adsorbed on the free surface of the virgin GAC, causing the iodine number to even deteriorate during supercritical fluid regeneration.

The complete desorption of the basic layer of about 18 mass percent should restore the surface of the exhausted GAC, resulting in an increase in the iodine number. To check this, iodine number determinations were performed on three samples with high mass loss. The anticipated tendency of increasing iodine number with increasing mass loss was indeed observed, though the extent of increase was disappointing. Compared to the iodine number of a pure virgin sample (1043) and exhausted sample (597) of F300, it was only possible to increase the iodine number by 4%. This can be explained by assuming that the thermal regeneration causes a burn-out of the micropores, which deteriorates the adsorption capacity of the GAC with each exhaustion/regeneration cycle. Thus, once an activated carbon sample is thermally regenerated, regeneration with *sc*-CO_2 is not a viable option anymore. The significant mass loss encountered with the F300 sample may be attributed to a modification of the active surface caused by thermal regeneration.

6. EVALUATION

6.1 Overview of Achievements

In this investigation three different "real-world" GAC samples, which had been exhausted in three totally different water purification installations in southern Africa, were investigated for regeneration by *sc*-CO_2.

The term "real world" should be understood in terms of the differences between the exhaustion processes applicable to activated carbon under typical industrial and/or environmental conditions in a given application (e.g. water purification), on the one hand, and activated carbon used in experimentation in the research laboratory under clinical conditions, on the other hand. These differences are briefly summarised below.

As far as clinically exhausted samples are concerned, they are exhausted within a few hours under optimum conditions. Generally only a few different contaminants from a highly concentrated solution are adsorbed onto the surface. Due to the high concentration, the energy of adsorption is quite low and the time of exhaustion fairly short. Under these circumstances even capillary condensation may occur. This means that many contaminants simultaneously reach the same pores or capillaries and thus cause the vapour pressure in the pores to rise to such an extent that the contaminants simply condense within the pores instead of being adsorbed onto the surface. In view of all these considerations, adsorbed contaminants may be removed fairly easily from the surface of such clinically exhausted samples.

The real-world samples are exhausted over an extensive period of time (several months), a large variety of contaminants in minute concentrations may be involved, biological growth on the surface may occur and the conditions for adsorption may vary significantly as a result of seasonal changes (moderate in summer, harsh in winter). Thus a selective adsorption of contaminants occurs, depending on the amount of energy released. In addition, the effect of ageing of the adsorbed species can deteriorate subsequent regeneration. In view of these considerations, it is understandable that much energy is needed to desorb components from the surface of real-world samples.

The only one of the three available real-world samples which resembles a clinically exhausted sample is the F400 from the Zuikerbosch Pumping Station, since it only stayed in the adsorption column for about 100 hours (i.e. a short adsorption time applies), it was employed to purify filter backwash water (i.e. a high concentration of contaminants prevails) and the temperature, light intensity, etc. hardly varied (i.e. constant environmental conditions exist). This GAC could be successfully regenerated by *sc*-CO_2 to the same extent (over 92% recovery of the original adsorption surface) as a clinically exhausted sample regenerated in the same way as in a previous investigation [3].

The two remaining samples represent true real-world samples of two distinctively different types.

The F300 from Goreangab Reclamation Plant had been thermally regenerated before regeneration with *sc*-CO_2 was attempted. There were no exhausted samples available from this water purification plant that had not been thermally regenerated before, since virgin and thermally regenerated activated carbon are always mixed on reloading the purification columns. In this case, treatment with *sc*-CO_2 resulted in a successful removal of "dead" material from the surface to the extent of a mass loss of more than 20%, though without recovering active carbon surface as shown by an incapability to simultaneously increase the iodine number. The mass loss versus time curve (figure 14) for the extraction attempts with *sc*-CO_2 bears witness of the removal of a double layer of adsorbed material, suggesting that previously adsorbed contaminants burnt onto the surface during thermal regeneration resulted in multiple layers of "dead" material. The removal of this "dead" material by *sc*-CO_2 is possibly facilitated by the destruction of the micropores of the carbon by repeated thermal regeneration and a consequent modification of the active surface sites. The results emphasise the necessity to check the recovery of active surface by iodine number determination after thermal regeneration. An increase in iodine number might be the result of reactivation instead of regeneration and a direct comparison to the results obtained by supercritical fluid regeneration (which is by no means a reactivation method) would be unfair.

The detrimental effect of thermal regeneration on subsequent supercritical fluid regeneration attempts was also recently shown for GAC used in the sugar refining industry. The comparison chart in Figure 15 indicates how the efficiency of *sc*-CO_2 regeneration compares favourably to that of thermal regeneration for samples which have not been thermally regenerated before (K 001 - K 003), but how it decreases for samples subjected three times (K 011) and eight times (K 022) to thermal regeneration prior to treatment with *sc*-CO_2.

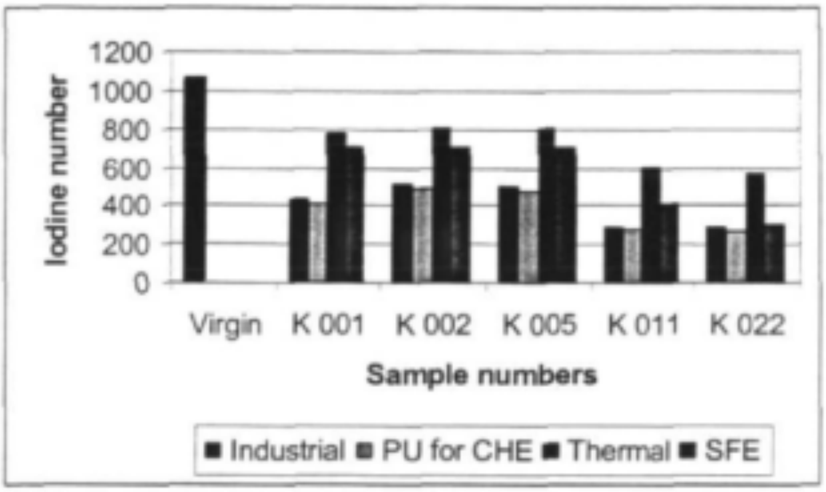

Figure 15 SFE Results for GAC from Sugar Refining Industry

The F400 and Diahope samples from Umgeni Water Process Evaluation Facility had been exhausted over an extended period of time (18 months) and had not been thermally regenerated before. These samples, therefore, truly represent real-world samples and thus served as ideal probes for *sc*-CO_2 regeneration. However, these samples could be regenerated to only a limited extent (2-5% recovery of the original carbon surface), indicating that factors such as varying environmental conditions, type and concentration levels of contaminants, ageing of adsorbed species and microbial growth on the carbon surface adversely affect the success of supercritical fluid regeneration.

In all three cases the optimum conditions for regeneration with *sc*-CO_2 appeared to be 450 bar/150 °C, indicating a common mechanism of regeneration to apply throughout. The moderate value of the density (0.65 g/ml) under these conditions either suggests that desorption rather than dissolution mainly controls the extraction or that a compromise between high and low densities to effect both dissolution and desorption exists. An analysis of the different types of contaminants encountered with the three types of GAC samples and their possible influence on the regeneration attempts was not envisaged for this investigation.

Finally, a maximum temperature combined with a suitable high density is required for optimum regeneration by *sc*-CO_2. Since desorption seems to outweigh dissolution, temperature is the more crucial parameter for success. A high temperature provides sufficient energy to desorb adsorbed components, even when the density is too low to really support dissolution. Likewise, a high density results in a poor regeneration outcome at low temperatures due to a lack of energy to desorb components from the surface.

6.2 Future Perspective and Recommendations

There are three perspectives forthcoming from this investigation which may be directive for future research in this field.

Firstly, the *sc*-CO_2 regeneration of real-world GAC samples is not promising enough to investigate economical viablility on an industrial scale. The important process requirements to be met include that (a) the GAC has not been thermally regenerated before, (b) the period of exposure is strictly limited, (c) the concentration levels of contaminants are not too low and (d) a combination of suitable conditions is maintained to ensure that both desorption and dissolution occur. However, *sc*-CO_2 regeneration may be considered for application in smaller-scale industries, such as a sugar refinery, where the above-mentioned requirements are more readily met and where initial high capital lay-out may be offset by lower running costs in the long term and a willingness to invest in environmentally friendly and regulatorily acceptable processing.

Secondly, attention was drawn to the inherent disadvantages of supercritical fluid regeneration (lack of energy supply to desorb adsorbed substances effectively) and of thermal regeneration (burn-out of micropores, modification of surface sites, formation of "dead" material in multiple layers). A possible future approach could be to combine the advantages of supercritical fluids (high solvent strength, high diffusibility) with the advantages of thermal regeneration (desorption without internal burn-out of micropores) to supply sufficient energy for successful regeneration.

Finally, the results obtained for the three types of GAC samples were all different, indicating that a generalised outsay on the viability of supercritical fluid regeneration is impossible and that each case should be dealt with and evaluated on its own.

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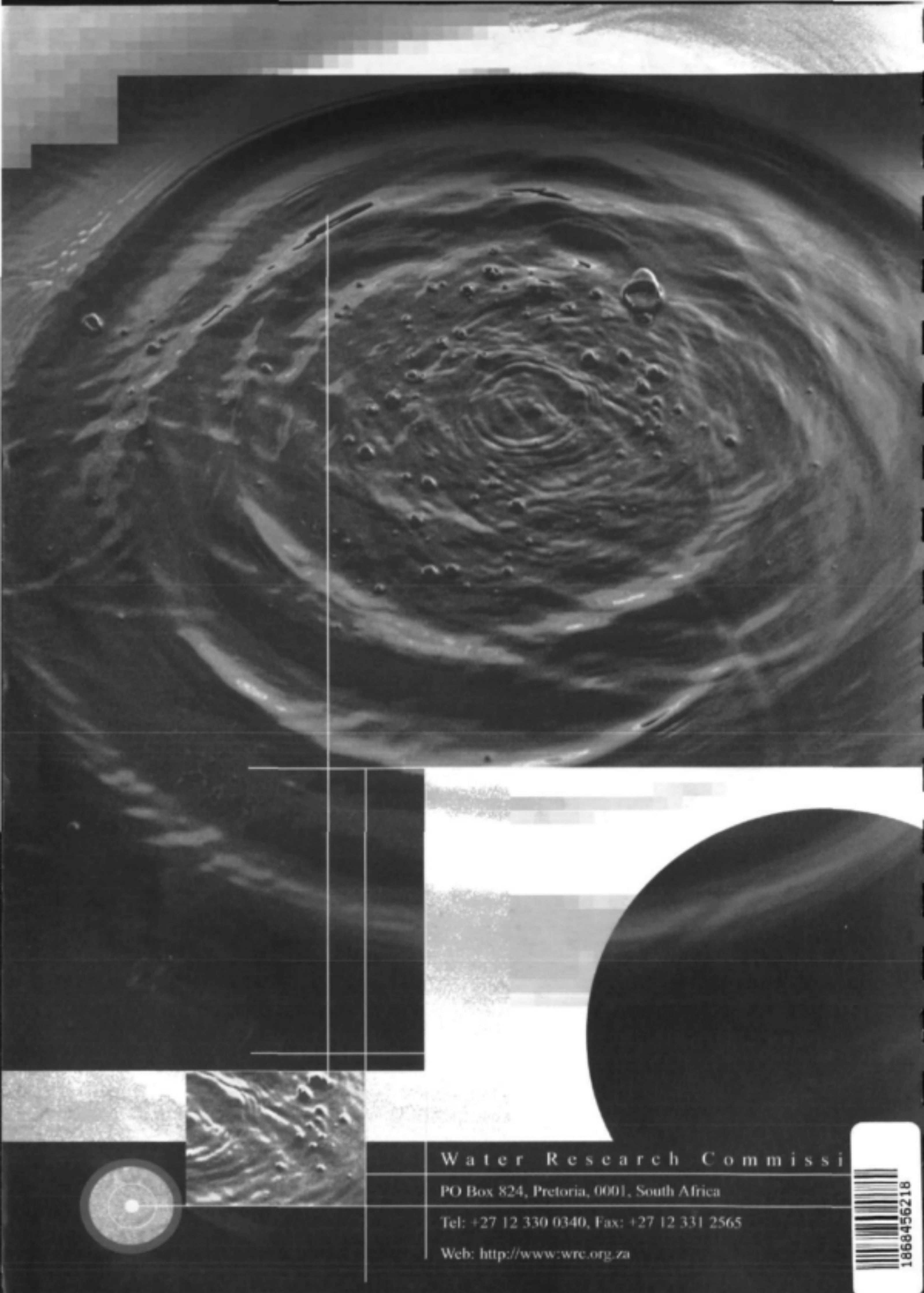

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