THE INTERACTION BETWEEN FREE CYANIDE AND SILVER IMPREGNATED ACTIVATED CARBON IN A COLUMN CONFIGURATION

BY

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A THESIS SUBMITTED IN FULFILMENT OF THE MASTERS
DEGREE OF TECHNOLOGY IN CHEMICAL ENGINEERING AT
THE CAPE TECHNIKON

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CAPE TECHNIKON
JUNE 2000

ABSTRACT

Due to equilibrium constraints and the relatively slow kinetics of the cyanidation of gold ores, calcium or potassium cyanide is added to the leaching stage in excess to that required theoretically. This, in many situations, result in large concentrations of free cyanide present in the effluent streams from gold plants. In view of the toxicity of cyanide and the fact that cyanide is fatal in small dosages, authorities have been forced to tighten up plant discharge regulations. Therefore, it is vital to remove cyanide from industrial effluent, not only to meet standard requirements, but also to recover the cyanide as a means of reducing chemical costs. The aim of this study is to recover, rather than destroy, free cyanide from effluent streams via a metal impregnated carbon-in-column configuration. The first part of the study focused on the mechanism of free cyanide recovery by metal impregnated carbon and the factors influencing the kinetics of the process in a batch reactor. The second part concentrates on the optimisation of such a process in a column configuration, and subsequently to recover the cyanide from the carbon.

In the batch experiments, it was found that impregnated metal carbon outperformed virgin carbon for free cyanide removal both from a kinetic and equilibrium point of view. Furthermore, the presence of other metal cyanides in solution with free cyanide has a negligible effect on the performance of the metal (silver) impregnated activated carbon to remove free cyanide. Moreover, scanning electron micrographs revealed distinct differences in appearance of metal impregnated carbons, which ultimately responds differently to the removal of free cyanide.

Although the kinetics of adsorption in the column experiments was found to be slower when compared to that experienced in a batch reactor, preliminary results show that a column configuration could be suitable for free cyanide recovery on a large scale. Furthermore, a sensitivity analysis, using the kinetics of adsorption and equilibrium cyanide loading as criteria, has been conducted on the column configuration. In these studies the effects of different bed volumes, competitive adsorption with other species present, different flow rates, different column diameters and initial cyanide concentrations on the process have been evaluated. These results were plotted as break-through curves, and the mass transfer zone (MTZ) was determined.

It was found that impregnation in an air atmosphere yields a product with a higher capacity than in a nitrogen atmosphere, compromising carbon through combustion. Under a nitrogen atmosphere a more robust product is formed. As can be expected, lower linear velocities and/or larger bed volumes as well as lower initial free cyanide concentrations improve the fraction of cyanide removed in a column configuration.

ACKNOWLEDGEMENTS

The work contained in this thesis was carried out in the Department of Chemical Engineering at the Cape Technikon between January 1998 and October 1999.

I would like to thank my supervisors, Mr Coetzee and Prof Petersen, for their guidance and support throughout this project.

I would like to thank MINTEK and the NRF for their financial support of this project.

A special thank you to my family for their support and especially my mother for her help with the typing of this work.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 ACTIVATED CARBON

1.1.1 Background

Carbon occurs abundantly in nature in the free state as coal. It is also known as charcoal, active or activated carbon, bone char and animal char. It has a highly porous structure and the internal surface area is readily accessible [1]. Activated carbon is used widely in industry and through the activation of the carbon, its physical properties are enhanced and its uses increased [1].

Activated carbon is prepared by the carbonization and activation of various raw materials, including coconut shells, agricultural byproducts, lignite, wood, peat and bituminous coal [2, 3]. Coconut shell activated carbon yields a better overall performance compared to other raw materials with the adsorptive capacity per volume as measure [2].

1.1.2 Manufacture of activated carbon

Almost any carbonaceous material can be used in the production of activated carbon [4]. During activation, the relatively inert carbon is transformed to a highly adsorbent form. It obtains high adsorptive capacity, mechanical strength and chemical purity [1].

1.1.2.1 Carbonisation

Carbonisation of the raw material takes place at between 500 °C and 600 °C in the absence of air. The raw material has a total surface area of only a couple of m^2/g [5]. During this process the non-carbon elements are removed and the remaining carbon atoms are arranged in organized elementary graphitic crystallites [5]. At this stage the carbon still has a relatively low adsorptive capacity, but it can be improved through activation with steam or carbon dioxide [6].

1.1.2.2 Activation

The three factors influencing the surface chemical and adsorptive properties of the carbon are:

- The nature of the starting material
- The composition of the activation atmosphere
- The duration temperature of the activated carbon. [5]

Chemical activation:

Chemical activation is carried out at lower temperatures than physical activation (between 400 °C and 1000 °C) [7]. Raw materials that are rich in volatiles are usually used in this process. They are treated with an activation agent that causes the formation of smaller sized elementary crystallites, which in turn promotes the development of a porous structure [5]. Some of the activation agents are $ZnCl_2$, H_2SO_4 and H_3PO_4 [7], as well as OH, K_2S and KCNS [5].

Physical activation:

In this method, the treatment of the carbon takes place in the presence of steam, air, CO_2 or a combination of these oxidising agents. Because of the high temperatures at which this is done (800 °C to 1000 °C), a product with a larger micropore volume is created. These sites are ideal for adsorption [8]. Activation takes place in two steps:

- The closed and clogged pores between the crystallites are freed by burning the disorganised carbon. Burn-off is kept below 10%, but increased porosity can be achieved through more burn-off. This is determined by the mechanism of carbon removal [5].
- Further activation causes the burning of the elementary crystallites [5] and the microporous structure of the carbon is developed [7].

1.1.3 The structure of activated carbon

Activated carbon has a microcrystalline structure that closely resembles that of graphite [6,7]. Some investigators have showed that this structure is necessary for adsorption [9], while others indicated that it is the most important factor in adsorption [10].

In the activated carbon the carbon atoms are held in a hexagonal arrangement in flat planes by covalent linkages. Two or more of these planes stacked on top of each other forms a crystallite [11]. The pore structure of the carbon is due to the irregular shaped spaces and large openings between the microcrystallites. The pores are classified according to their diameters as follows [4]:

- Macropores : 500 – 20000 nm
- Mesopores : 5 – 500 nm
- Micropores : 8 – 100 nm

The structure of the pores is determined by the source material used, as well as the activation procedure and extent of activation [12]. The openings are formed by burnout of vulnerable areas of carbon and binder materials that formed the source material [13]. The macropores do not play a major part in the adsorption, but do enable the molecules of adsorptive material to reach the smaller pores in the carbon particle [2,14]. This is where the adsorption takes place, mostly in the micropores. They constitute the largest part of the activated carbon's internal surface area. This surface area can be between 600 and 1500 m^2/g [15].

The other factor determining the activated carbon's adsorptive properties, together with its porous structure and surface, is its chemical composition. The activation conditions determine the nature of surface functional groups on the carbon [2]. These functional groups affect the adsorption of organic compounds onto the carbon [16]. The surface consists mostly of basal and graphitic planes, where the edges of the graphitic planes form the sides of the microcrystallites. It is here that various functional groups can be found to yield a more heterogeneous form [2]. No functional groups would be found on the basal planes, as they are already relatively uniform. Only a small section of the total surface area will have functional groups, but variations in their composition can have an influence on the activated carbon's performance.

1.1.4 Use of activated carbon as an adsorbent

Numerous authors have investigated the adsorption of metal cyanide onto activated carbon [12, 17, 18, 19, 20, 21]. Different mechanisms for this reaction have been proposed, but little agreement could be reached regarding this phenomenon. The reasons for this disagreement are:

- Identification of the different species is very difficult due to the complexity of the carbon surface.
- Different carbons have been used
- Different experimental conditions have been used in the various studies [12]

The five main categories in which all published gold cyanide adsorption mechanism can be placed are:

- Adsorption as $M^{n+}(Au(CN)_2^-)_n$ [18, 19, 22, 23]
- Adsorption as $M^{n+}(Au(CN)_2^-)_n$ followed by partial reduction [24]
- Adsorption of $Au(CN)_2^-$ followed by partial degradation to AuCN [25, 26]
- Adsorption in an electrical double layer [11, 27]
- Adsorption on the graphite structure [28, 29]

1.1.5 The Carbon-in-Pulp process

This process is in use since 1961 [30] for the recovery of gold and silver. In the process, dissolved gold in a cyanide environment as well as cyanide in the adsorption and elution sections, are used. This method has the following advantages [31]:

- Decreased capital costs
- Decreased operating costs
- Improvement in gold recovery
- Reduced sensitivity of recovery to throughput rate
- Ability to handle shaley and clayey ore more efficiently than by filtration

Unfortunately, large quantities of cyanide are present in the effluent leaving the plant.

1.1.6 Uses of Activated carbon

Activated carbon has been used since 3000 years ago for the purification of water [3]. The Greeks also used it for medicinal purposes [1].

Using activated carbon for filtration is a cost effective water treatment process. It is used to remove volatile organic compounds, soluble organic compounds and other materials that can be adsorbed. This ability is due to the carbon's large surface area [3].

1.2 CYANIDE

1.2.1 Background

The term cyanide, or free cyanide, is used for the CN^- anion or its acidic form, HCN (hydrogen cyanide). Cyanogen, C_2N_2 is formed by oxidation of cyanide ions and a simple cyanide refers to a compound that dissociates to CN^- and the cation, e.g. NaCN to Na^+ and CN^-. A nitrile is an organic compound containing cyanide, and one that liberates the cyanide ion during metabolism, is called a cyanogen. They can be simple or complex [32]. The classification of cyanide and cyanide compounds in cyanidation solutions on the basis of stability can be seen in Table 1.1.

The cyanide ion can be found in nearly all living organisms, which can tolerate or even need small quantities thereof. The fruits and seeds of many plants contain cyanogens capable of releasing free cyanide after enzymatic degradation. The combustion of materials containing carbon and nitrogen (as well as some plastics when burned) has the potential to form cyanide. The different cyanides find applications in diverse fields such as chemical synthesis, electroplating, mineral extraction, dyeing, printing, photography, agriculture and the manufacture of paper, textiles and plastics [32].

Numerous methods for the analysis of cyanide and its complexes have been studied [33, 34, 35, 36, 37, 38]. Despite the many analytical methods available, only a few can produce accurate and reliable results.

The toxic cyanide solutions involve a combination of constituents such as metal cyanide complexes and free cyanide. Knowledge of these solutions is of importance in establishing procedures to limit the impact of mining operations on the environment [39].

1.2.2 The cyanidation process

This forms part of the process to extract gold from its ore. It is highly efficient and recovery of small amounts of gold is possible [39]. Cyanide also forms complexes with many other metals [9]. This complexity of cyanide solutions creates difficulties in wastewater treatment and chemical analysis, but due to its availability and the strength of its complex with gold, it is used for ore processing.

1.2.3 Cyanide complexes

The different cyanide complexes that are formed in gold processing circuits or cyanide solutions and effluents can be divided into five categories [40]. These include free cyanide and the metal complexes it forms (Table 1.1).

1.2.4 The environmental impact of cyanide

Cyanide can form 72 different metal complexes from 28 elements [41]. These complexes vary in solubility and stability and can therefore release cyanide into the environment. However, the metals that form a strong complex with the cyanide, can be used to remove free cyanide [42, 43, 44].

Eight main mechanisms that determine rate and toxicity of cyanide in the environment are [45]:

- Complexation (chelation) – many of the transition metals chelate or complex with cyanide, which results in the formation of metal cyanide compounds that are less toxic than free cyanide.

- Cyanide complex precipitation – some iron cyanide complexes form 'insoluble salts with, including amongst others, iron, copper, nickel and silver. Within the soil environment, the oxidation potential would result in the formation of ferro cyanide precipitates. If sulphur is present within the soil, the iron-cyanide complexes can react with thiocyanate to form an even more stable complex.
- Adsorption – This is a mechanism that attenuates cyanide in soils.
- Oxidation to cyanate – cyanide is converted to cyanate when in the presence of strong oxidizers.
- Volatilisation – this involves the formation of HCN gas from cyanide and water.
- Biodegradation – once the cyanide salts move a short distance through the soil, they are biologically converted under aerobic conditions to nitrates.
- Formation of thiocyanate – free cyanide reacts with various forms of sulphur in the environment to form thiocyanate.
- The hydrolysis / saponification of HCN – HCN is hydrolysed to give formate as either formic acid or ammonium formate as the pH falls within the system.

The most important of these mechanisms is the volatilisation of HCN [46].

1.2.5 Toxicity of cyanide

It is a well-known fact that cyanide can produce harmful effects. The four forms of cyanide that exist in mining solutions are free cyanide, iron cyanides, weak and dissociable cyanides and cyanide related compounds. Cyanide as hydrogen cyanide can be absorbed by the body through ingestion or inhalation at a very fast rate. It is then carried to the plasma [39]. It can lead to asphyxiation and tissue death, failure of all vital functions and finally death. Immediate death is the result the acute toxicity of cyanide, but it and its complexes can have other long term effects such as impaired swimming ability, reduced reproduction, decreased growth and physiological abnormalities.

Less than 10 mg free cyanide ingested per day is non-toxic. When exposed to hydrogen cyanide in concentrations of 100 to 300 ppm, death can occur in 10 to 60 minutes. If this is increased to 2000 ppm, death will occur within 1 minute. The LC_{50} of free cyanide is 100 mg/kg of body mass [39].

The cyanide complexes can break down, releasing the free cyanide to the environment. This is the main concern from a toxicological perspective.

The silver cyanide complex is fairly stable at pH levels that are present in mine effluents. It is thus effective in reducing the free cyanide concentration in effluents. The silver ion is poisonous on its own, but the large quantities of free cyanide available in these effluents, promotes the complex forming [42].

1.2.6 The recovery of cyanide and its associated problems

The following processes have been employed to recover cyanide from effluent streams:

- The Mills Crow process used acidification, air stripping and re-adsorption [47].
- Between the 1930's and 1950's a method (pre-runner of the AVR process) yielding 93% recovery was used [48].
- The above process was improved in the 1970's. It makes use of acidification, volatilization and reneutralisation (AVR) [49]. 99% removal was possible.
- Packed towers were used for the AVR process, yielding 95% recovery, in the 1980's [50, 51].

Many studies on free cyanide removal focused on chemical treatment, biological treatment and natural degradation. All of these processes have either limiting operating conditions, or alternatively, expensive reagents are needed.

1.3 FREE CYANIDE ADSORPTION ONTO ACTIVATED CARBON

Mining plant effluents, especially the waste from gold mines, contain large amounts of cyanide that can contaminate the earth's water resources [52]. Pohlandt-Watson and Jones [53] found that most of the tailing dams analysed, contained more than 20 mg/L of cyanide. On average the amount of free cyanide in plant tailings is 60 mg/L. The General Effluent Standard limit is 0.5 mg/L.

The following methods are used in the destruction of cyanide:

- Oxidation by alkaline chlorination [54]
- Oxidation with ozone [55]
- Electrolytic decomposition [56]
- Enzymatic degradation [57]
- Detoxification by treatment with ferrous sulphate [58, 59, 60]

All these methods have major drawbacks such as high cost, undesirable byproducts and limited efficiency. The methods for cyanide removal are:

- Reverse osmosis
- Ion exchange
- Adsorption onto activated carbon

These methods fail to reduce the cyanide concentration to acceptable levels.

The adsorption of free cyanide onto both granular [61] and powdered activated carbon [62] has been investigated. When the adsorption occurs in an oxygen atmosphere, oxidation is detected [61]. The process is unaffected by the presence of nitrate, sulphate and chloride ions [62]. Guo *et al* [63] found that adsorption is slow when dilute cyanide solutions are contacted with granular activated carbon. According to Adams [64], wood-based carbon yielded the best results.

The efficiency of this process is low (the carbon content or agitation needs to be increased to impractical levels [63]. The use of a metal impregnated carbon was therefore proposed to increase recoveries.

1.4. FREE CYANIDE ADSORPTION ONTO METAL IMPREGNATED ACTIVATED CARBON

The various removal and destruction processes described earlier [65], can only reduce cyanide to ppm levels. This is not effective enough to meet the strict regulatory requirements. Expensive reagents, which cannot be reused, are also required. Van Weert and de Jong [66] investigated the use of silver impregnated carbon for the removal of cyanide. It is already known that cyanide and silver form a relatively strong complex that is easily adsorbed by activated carbon. This system has the following advantages:

- Cyanide is removed from the solution
- No oxidation products are left
- It is a selective process
- There are relatively low costs involved in the process
- It is compatible with the gold and silver mining practices
- It could be possible to reuse both the carbon and cyanide

Van Weert and de Jong [66] showed that silver impregnated activated carbon (SIAC) could reduce free cyanide levels from 150 ppb to below 5 ppb. This is a vast improvement on activated carbon. This is also the case at the ppm level [45].

The mechanism is explained via a number of theories [67]. The principle mechanism is as follows:

- Cyanide leaches silver from the carbon and forms $Ag(CN)_2^-$
- The complex is adsorbed back onto the carbon [68]

The rate-limiting steps were found to be the charge transfer and the diffusion of the reagents from the solution to the carbon surface [69]. The adsorption of the complex onto the carbon can be due to electrostatic interaction with the surface [70], adsorption as an ion pair or neutral molecule [71], or a multi-layer adsorption at the surface [72, 27].

Schlettwein [45] optimized the impregnation procedure for the manufacture of SIAC and achieved good results at the ppm level. A problem with this method, however, is that a large percentage (generally in excess of 50%) of the carbon is lost due to combustion in the furnace. Executing this method in a nitrogen atmosphere is proposed. This is further discussed in chapter 4.

1.5 FREE CYANIDE AND SIAC SYSTEM IN A COLUMN CONFIGURATION

Little work has been done on the performance of SIAC in a column configuration. Choi *et al* [73] have found that free cyanide can be reduced from 20 ppm to below 10 ppb with residence times of 4 minutes and no silver losses. For longer residence times, slight silver losses did occur. These tests still need to be scaled up in order to test possible commercialization.

Using a column configuration has obvious advantages:

- Continuous operation is possible
- Transfer of materials are limited
- Adsorption and regeneration can take place in the same unit

Although it is not possible to send slurries through a packed column, there are other applications for this system, for example heap leach processes.

1.6 OBJECTIVES

The performance of silver impregnated activated carbon in a batch configuration has been studied previously [68, 45] and it proved to be a vast improvement on virgin activated carbon. A method for producing an optimized SIAC has also been proposed [45]. Little work has been done on the implementation of this technology in a column configuration.

The objectives of this study were:

- To solve the problems concerning the current optimized carbon (loss of carbon due to combustion).
- To evaluate the performance of SIAC in a column configuration.
- To conduct a sensitivity analysis of the system to various operating parameters.
- To evaluate the viability of this system in practice.

Table 1.1 The classification of cyanide and cyanide compounds in cyanidation solutions on the basis of stability [40]

Classification	Compound
Free cyanide	CN^-, HCN
Simple compound:	
a) readily soluble	NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$
b) neutral insoluble salts	$Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$, AgCN
Weak complexes	$Zn(CN)_4^{2-}$, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$
Moderately strong complexes	$Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$
Strong complexes	$Fe(CN)_5^{4-}$, $Co(CN)_5^{4-}$, $Au(CN)_2^-$, $Fe(CN)_6^{3-}$

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 BATCH CONFIGURATION

2.1.1 The Mechanism

The free cyanide is removed from the solution via the following four reactions:

1. Free cyanide adsorbs onto the SIAC (silver impregnated activated carbon).
2. Silver is leached into the solution by the free cyanide.
3. Silver cyanide complex is formed.
4. The silver cyanide complex is adsorbed back onto the carbon.

Reaction number (1) occurs independent to the other three reactions. Reactions (2), (3) and (4) are the steps that are needed to remove the free cyanide using the impregnated activated carbon.

2.1.2 Reaction rate and controlling step

If the explained mechanism is used as reference, the following explanation of the reaction rates can be given:

The effect of (1) is assumed to be small, since it has been shown that the adsorption of free cyanide onto carbon is poor. (See Chapter 5). The influence of each of the other reactions need to be determined to find the overall rate-limiting step in the adsorption process. Analysis is normally based on the amount of free cyanide detected in the sample solution. This method does not measure the adsorption of the silver cyanide complex due to the fact that only free cyanide is detected. What is physically measured is the "disappearance" of free cyanide either via complex forming, or direct adsorption of the free cyanide (effects (1) and (3)).

The amount of silver in solution can be detected by means of atomic spectrophotometry. This only reveals the total amount of silver in solution and is not an indication of the form it is in at that specific time. Only an indication of the overall rate of adsorption can therefore be measured directly.

In this study the overall "disappearance" of free cyanide is used as a measure of the adsorption. However, it is possible that some of the "disappeared" cyanide is actually still present in the solution as a metal-cyanide complex. This was investigated and the effect can be significant, especially with longer residence times (see Chapter 5).

2.1.2.1 Calculation of overall reaction rate

The equation for determining the rate of cyanide adsorption (k_f) is derived from the material balance over the batch reactor as follows:

$$\frac{dC}{dt} = \frac{6 \times k_f \times m}{\rho \times d_p \times V}(C_{surface} - C) \qquad [2.1]$$

Furthermore, during the initial stages of adsorption the free cyanide concentration at the carbon surface ($C_{surface}$) is very small compared to the bulk concentration, thus:

$$\frac{dC}{dt} = \frac{6 \times k_f \times m}{\rho \times d_p \times V}C \qquad [2.2]$$

Integrating the above equation:

$$\ln\frac{C_i}{C} = \frac{6 \times k_f \times m}{\rho \times d_p \times V}t \qquad [2.3]$$

The slope ln C_i/C is plotted against time is used in equation 2.4 to determine the apparent rate constant of the adsorption.

$$k_f = \frac{slope \times \rho \times d_p \times V}{6 \times m} \text{ (m/s)} \qquad [2.4]$$

2.1.3 Calculation of capacity

The following equation is used to determine the amount of free cyanide which one gram of carbon will adsorb from solution:

$$\text{Capacity} = \frac{Ci - Ce}{m} V \text{ (mg CN}^-\text{/g carbon)} \qquad [2.5]$$

2.1.4 Silver loading

The method proposed by Bratzel *et al* [75] did not yield results (as explained in Chapter 3). Following their procedure yielded results of zero silver loading. The silver loading on the carbon was therefore calculated by means of the following mass balance equation (expressed as mass fraction):

$$\text{Loading} = \frac{Ci - C}{m} V \text{ (mg silver/g of carbon)} \qquad [2.6]$$

This equation calculates the amount of cyanide remaining on the carbon after adsorption.

2.1.5 Isotherm

The isotherm is an equilibrium expression that should describe the system accurately. It describes the relationship between the total capacity of the adsorbent and the equilibrium concentration of the adsorbed substance in the solution, under specific operating conditions. The most popular isotherms for single solute aqueous systems are [76, 77, 78]:

1. Linear isotherm - $q_e = AC_e$ [2.7]
2. Freundlich isotherm - $q_e = AC_e^n$ [2.8]
3. Langmuir isotherm - $q_e = \frac{AC_e}{B + C_e}$ [2.9]

In the Freundlich isotherm, the constant A is an indication of the maximum loading of the adsorbing material onto the adsorbent, for those conditions of temperature, pH and other operating parameters.

2.2 COLUMN CONFIGURATION

2.2.1 The breakthrough curve and mass transfer zone

Please see Figure 2.1 for reference.

As a feed solution passes through a column, an adsorption wave is formed and no contaminant is found in the exit stream. The topmost part of the column will be saturated first (in the case of gravitational flow). Just below that, will be a region where adsorption is taking place. This is called the mass transfer zone (MTZ). Below that, to the end of the column, the adsorbent will be relatively contaminant free.
With time the mass transfer zone moves through the column to the exit. When it starts moving through the exit, contaminant starts to exit the column. This is called the

breakpoint and can be seen on a breakthrough curve at the point where the exit concentration of contaminant starts to rise from zero. (The breakthrough curve is a plot of exit concentration against time or number of bed volumes.) The mass transfer zone can be calculated from these curves as a simple ratio: time from breakpoint to saturation against total running time multiplied by the bed height. This theoretical process is described by Treyball *et al* [74]. It should be remembered that in practice, there would not be sharp boundaries between the different sections. The different zones will merge into each other.

2.2.2 The reaction rate

The liquid phase mass balance yields the following equation:

$$\frac{dC}{dt} = \frac{6 \times k_f \times m}{\rho \times d_p \times V \times \varepsilon}(C_s - C) \qquad [2.10]$$

It can be assumed that film mass transfer determines the adsorption rate in the early stages. It can also be assumed that the cyanide concentration on the carbon surface is negligible compared to that of the bulk solution. Equation 2.10 will then simplify to:

$$\frac{dC}{dt} = -\frac{6 \times k_f \times m}{\rho \times d_p \times V \times \varepsilon} \times C \qquad [2.11]$$

Integrating Equation 2.11 give:

$$\ln\frac{C_0}{C} = \frac{6 \times k_f \times m}{\rho \times d_p \times V \times \varepsilon} \times t \qquad t \to 0 \qquad [2.12]$$

When the column height is not sufficient to contain the whole concentration wavefront, the initial stages of the breakthrough curve will be determined by film transfer alone. The apparent rate constant of adsorption (k_f) can then be determined by:

$$k_f = \frac{\ln \frac{C_0}{C_t} \times V \times d_p}{6 \times (1 - \varepsilon) \times A \times H} \qquad [2.13]$$

2.3 OPERATING CONDITIONS

2.3.1 Linear velocity vs. volumetric flow rate

In the column-configuration linear velocity of the solution is used as a control parameter rather than the volumetric flow rate. This is due to the fact that different column diameters can easily be compared when the same linear velocity is used. This is not the case when using the volumetric flow rate. The linear velocity is calculated by dividing the volumetric flow rate by column cross-sectional area.

2.3.2 Column diameter

When the column diameter is relatively small compared to the average particle diameter, wall effects will influence the result. The general rule of using a column with a diameter of at least 20 times that of the carbon was used for the sensitivity analysis of the silver impregnated carbon reduced in air (average particle diameter of 1.8 mm and a column diameter of 37 mm).

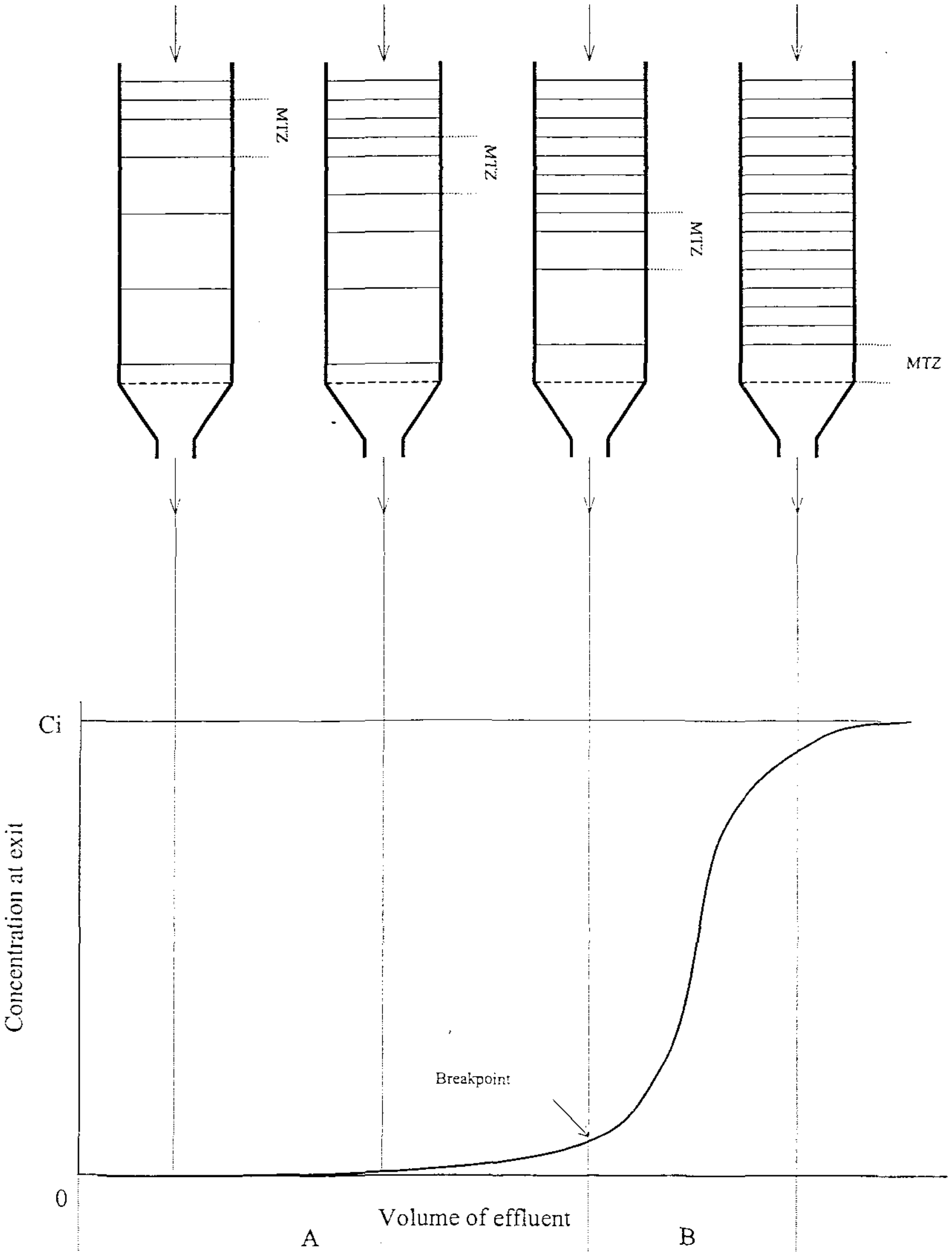
2.3.3 Carbon characteristics

The column experiments were conducted in a packed bed configuration. Initially, both gravitational and up-flow were tested, but it was decided to conduct the bulk of the experiments using gravitational flow. It has the advantages of more controllable flow patterns and the possibility of fluidization is eliminated.

However, it was found that this method could limit the maximum flow rate through the bed. This will have an effect in the following circumstances:

1. When small particle sizes are used, these will block the channels needed for the flow.
2. When the impregnated carbon reduced in air is used. These particles are brittle and the loading of the column will produce fines, which will block the column.

Figure 2.1 The mass transfer zone in a column and corresponding breakthrough curve [74].



$$\boxed{MTZ = B/(B \div A)*H}$$

CHAPTER 3

EXPERIMENTAL

3.1 BATCH EXPERIMENTS

All batch experiments were conducted in 1L reactors with three evenly spaced baffles. Overhead stirrers were used with a constant agitation rate of 300 rpm. At this speed all solid particles were in suspension with minimum breakage caused by the impeller. The dimensions were as follows:

- Perspex reactors:
    - Internal diameter = 11 cm
    - Height = 15 cm
    - Baffle width = 1 cm
- Impeller:
    - Impeller type = flatblade
    - Width = 6 cm
    - Height = 5 cm

All the reactors were covered with Perspex lids to prevent losses due to evaporation.

3.2 COLUMN CONFIGURATION

In all the experiments conducted in the column configuration, the cyanide selective electrode was used to determine the amount of free cyanide present in the effluent. This data was used to derive breakthrough curves, which in turn was used to determine the properties of the system. Three different column diameters were used:

1. 23 mm internal diameter – sensitivity analysis using air impregnated carbon.
2. 38 mm internal diameter – sensitivity analysis using N_2 impregnated carbon.
3. 68 mm internal diameter – to test the sensitivity to a change in column diameter.

A positive displacement pump was used to generate flow through the column. A 25 L storage drum was used for the source stream. Samples were taken according to either time or bed volumes of effluent through the column.

3.3 IMPREGNATION PROCEDURE

In the impregnation process 15 g of washed carbon was contacted with a 1L solution of a silver cyanide complex: 98% Potassium dicyanoargentate- $KAg(CN)_2$.

The method proposed by Schlettwein [45] includes the following steps:

1. Cleaning the carbon by boiling it in distilled water for 1 hour to remove fines and entrapped air.
2. Adsorption of Ag as $Ag(CN)_2^-$ onto the clean virgin carbon with a contact time of 15 hours. The Ag/carbon ratio was 1 liter of a 1000 ppm Ag solution contacted with 15g of carbon.
3. Decomposition of the silver complex to silver metal was done in a furnace for 5 hours at 300°C. An air atmosphere was used.

Choi *et al* [68] described a similar procedure for the impregnation.

The method proposed in this work adds another step at the start to break off most of the irregular edges on the particles. This is done by vigorous agitation for 1 hour. The Ag concentration is also lowered to 500 ppm and the decomposition step executed in a nitrogen atmosphere (2 hours at 700°C).

3.4 MATERIALS AND EQUIPMENT

A coconut-shell carbon, with average particle size of 1.7 mm and density of 1248 kg/m^3, was used. For analysis of the silver, an atomic absorption spectrophotometer was used and for cyanide, a cyanide selective electrode with an EA920 ion analyzer and reference electrode. The silver loading on the SIAC prepared in Nitrogen is 2.3%. The SIAC prepared in air lost mass due to combustion, thereby reducing the density. The use of this type of SIAC was discontinued. Perspex batch reactors with three baffles were used for these experiments. Three different column diameters were used: 25 mm, 37 mm and 68 mm. These were glass columns, tapered at the bottom and fitted with a tap and a cross-sectional glass partition to support the carbon bed.

3.5 ANALYTICAL PROCEDURES

3.5.1 Cyanide analysis

Free cyanide was analyzed using a cyanide sensitive electrode, combined with a reference electrode, connected to an EA 920 ion- analyzer. For the electrode to function properly, the ionic strength had to be adjusted using a 0.1M solution of NaOH. This also increased the pH to 11.Only the first two significant figures were used due to instrument limitations and time constraints.

3.5.2 Silver analysis

Silver in solution was determined by means of an atomic absorption spectrophotometer and hollow cathode lamp.

3.5.3 Silver loading

It was attempted to determine the silver loading on the carbon by using the method proposed by Bratzel *et al* [75].

The procedure is as follows:

1. Ash the carbon.
2. Add aqua regia and then heat the mixture until all the liquid has evaporated. Repeat this process with aqua regia and a third time with concentrated HNO_3. Do not let all the liquid evaporate the last time.
3. Filter the product with 5% HNO_3
4. Read the concentration.

No silver was found on the carbon by means of this procedure. The silver loading on the carbon was then determined using by difference over the adsorption step in impregnation. It was calculated at 2.3% by mass. The dissolved concentration was detected by means of an atomic absorption spectrophotometer and hollow cathode lamp.

CHAPTER 4

IMPREGNATION

The term silver impregnated activated carbon refers to activated carbon with silver metal attached to it. This is achieved by, firstly adsorbing a silver-cyanide complex onto the carbon, and then thermally reducing this compound to silver metal. The main factors that influence the final product, are:

- Silver concentration in solution – Higher initial concentrations of silver, will increase the silver loading of the product.
- Adsorption time – The system needs to be at equilibrium to ensure maximum loading of silver.
- Agitation – Keeping the solid particles in suspension enhances the adsorption rate. This is closely linked to the step mentioned above.
- Temperature in reduction step – When the temperature is too low, the reduction of the complex to silver metal, will not be completed. The process will also take longer at lower temperatures.
- Atmosphere in reduction step – This have a large influence in the quality of the SIAC and reduction in either an air atmosphere, or in a Nitrogen atmosphere is discussed in detail in this chapter.
- Other influences – Cyanide can be destroyed by light (in the adsorption step). The SIAC will also absorb water from the atmosphere, especially when hot. This will increase the mass without any other benefits to the process.

Firstly, the method previously used for the manufacture of silver impregnated carbon and the problems associated with it will be explained. A new method is then proposed.

4.1 RESULTS IN AIR ATMOSPHERE

The results from batch experiments when the impregnated carbon was prepared in an air atmosphere can be seen in Chapter 5. In a 24-hour experiment (using an initial free cyanide concentration of 20 ppm) in a 1L batch reactor, 1g of impregnated carbon adsorbed 12 mg of free cyanide. The isotherm result is explained in Chapter 5.

However, a major drawback of this procedure is that a large percentage (up to 60%) of the carbon mass is lost through combustion. The product is also soft and brittle.

It was therefore attempted to execute the reduction step of the impregnation in an inert atmosphere.

4.2 N_2 ATMOSPHERE OPTIMIZATION

Another step was added to the impregnation procedure. After cleaning, the carbon was agitated aggressively for two hours to remove the sharp edges off the carbon to yield a more regularly shaped product. This was done to prevent these edges breaking off in later stages of impregnation, causing unnecessary fines that will go to waste. This did not have any effect on the capacity of the SIAC reduced in air – the carbon became brittle and broke up into fines after in the furnace step as before.

The results of the nitrogen optimization can be seen in Table 4.1. Temperature and time in the furnace were varied and the resultant impregnated carbon used in a standard batch experiment to determine the capacity. The optimization of the impregnation procedure is, however, not the aim of this investigation and it is therefore possible to improve on these results with further experimentation.

As can be seen from Table 4.2, the impregnated carbon produced in nitrogen atmosphere has a much lower capacity compared to the impregnated carbon produced in an air atmosphere (6 mg/g vs. 12 mg/g carbon). The carbon is, however, much more robust and this is an important quality when the transfer of the product is considered. The results of the isotherm tests are discussed in Chapter 5.

The large difference in the capacities could be attributed to the effect of the much larger surface area available for adsorption when decomposition occurs in air.

1. After combustion, the carbon has a lower density and therefore a greater volume (and surface area) per gram.
2. When agitated the carbon produced in air breaks up into fines, yielding a larger surface area. This does not occur when a nitrogen atmosphere is used.

The carbon produced using a nitrogen atmosphere during the thermal decomposition step was used in the final column tests.

4.3 $KAg(CN)_2$ CONCENTRATION

As can be seen from Table 4.3, the concentration of silver used in the impregnation step has a large influence on the capacity of the impregnated carbon. When the concentration was doubled to 1000 ppm Ag, the capacity doubled to 12 mg/g of carbon. The maximum for this trend was not determined.

4.4 ACTIVE GROUPS ON CARBON

The impregnated carbon was contacted with 500 ppm Ag as $Ag(CN)_2^-$ under the same conditions as in the impregnation procedure. The adsorption of Ag onto the impregnated carbon followed the same trend as the adsorption onto virgin activated carbon (Figure 4.1). The active groups seem to be available again after the decomposition of the silver complex.

This is the same as reported by Choi *et al* [68] and Schlettwein [45] for the silver impregnated carbon produced in an air atmosphere.

Table 4.1 Optimisation of Nitrogen atmosphere condition in impregnation

- 500 ppm $KAg(CN)_2$ used for impregnation step.

Ci	C	time(h)	temp.(C)	capacity(mg/g)
14	12	5	250	2
14	12	0.5	300	2
20	17	2	500	3
13	10.5	0.5	500	2.5
19.5	13.5	4	700	6
20	**14**	**2**	**700**	**6**

Table 4.2 Comparison between the cyanide capture capacities of the different carbons

Virgin Carbon	Air SIAC	N_2 SIAC
1-2 mg/g	12-14 mg/g	6 mg/g

Table 4.3 Effect of $KAg(CN)_2$ concentration on cyanide capacity

Concentration	N_2 SIAC capacity (mg/g)
500	6
1000	12

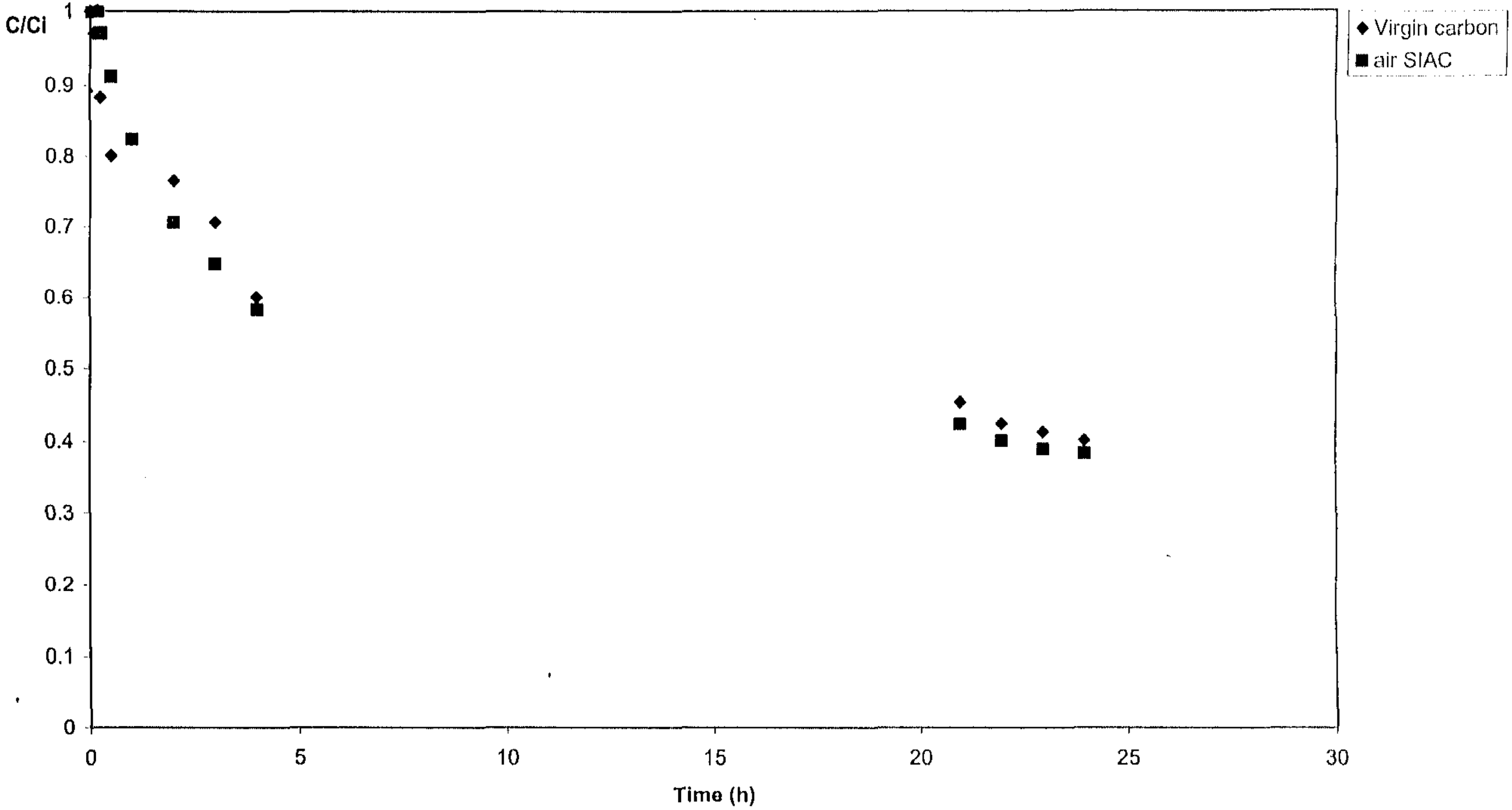


Figure 4.1 Adsorption profile of silver cyanide onto virgin carbon and air SIAC
[500 ppm $KAg(CN)_2$ in solution]

CHAPTER 5

ADSORPTION OF FREE CYANIDE IN A BATCH CONFIGURATION

5.1 MECHANISM

The mechanism proposed by Choi *et al* [68] and Schlettwein [45] seems to be appropriate for both types of impregnated carbon. This was explained in Chapter 1 and the steps are briefly repeated here:

- Cyanide leaches silver from the carbon and forms $Ag(CN)_2^-$
- The complex is adsorbed back onto the carbon [68]

The kinetic properties of the steps within this reaction are not known.

5.2 ADSORPTION TESTS

The tests were performed in 1L batch reactors for a period of 24h at an initial bulk concentration of 20ppm. 1g of adsorbent were used. The pH was increased to 11 and the contents of the batch reactor were agitated at 300 rpm using a flat blade impeller. All tests were executed at room temperature.

A comparison between the capacities of virgin activated carbon, silver impregnated activated carbon reduced in air and silver impregnated activated carbon reduced in nitrogen, can be seen in Table 4.2. Figure 5.1 shows the comparison of virgin activated carbon and the silver impregnated activated carbon reduced in air.. From this table, it is clear that both forms of impregnated carbon are superior to the virgin carbon. While the virgin carbon has a capacity of only 1-2 mg/g of carbon under these conditions, it increases to 6 mg/g for the impregnated carbon reduced in nitrogen and 12-14 mg/g for that reduced in an air atmosphere. The impregnated carbon reduced in an air atmosphere also outperforms that reduced in nitrogen. This was explained in Chapter 2.

Isotherm tests were done to compare the equilibrium conditions for these carbons.

5.2.1 ISOTHERMS

In these isotherm tests, 0.5 or 0.20 grams of the carbon was added to each of five batch reactors containing between 5 and 25 ppm free cyanide. The reactors were agitated for 72 h and the final concentrations were measured

It must be remembered that, due to the analytical method used, the loss of free cyanide is measured and not the actual adsorption of the free cyanide. It must also be remembered that there are actually four different reactions taking place simultaneously (described in Chapter 2). Varying results were achieved, depending on the exact state of the system when the samples were taken. Therefore, the isotherms can only be used as a guideline.

Taking the above into account, both types of impregnated carbon seem to resemble the Freundlich isotherm model the closest. This can be seen by the fact that the predicted A values for the two tests for each carbon was very similar (16,7 & 17,8 for air impregnated carbon and 5,2 & 6,1 for nitrogen impregnated carbon). The slight difference in the values for the two experiments can be attributed to external factors, including the sensitivity of the cyanide electrode. The specific data points and n values differed quite radically, which confirm the fact that no single isotherm equation can describe the system completely.

The carbon reduced in nitrogen achieves its maximum predicted capacity (A) already at low levels of initial bulk concentration (Figures 5.2 & 5.3) In Figure 5.3 the last

two data points seem to be influenced by external factors such as measurement faults or a shift in the calibration of the cyanide electrode.
The A values for the SIAC reduced in air, was calculated as 17.8mg/g and 16,7mg/g. This is considerably higher than that of the SIAC reduced in nitrogen, but a higher initial concentration is needed to achieve this maximum value. The plot of Qe vs Ce can be seen in Figure 5.4 and Figure 5.5.

The results of the isotherm tests and the equilibrium equations are tabulated in Tables 5.1 and 5.2 for nitrogen atmosphere and Tables 5.3 and 5.4 for air atmosphere.

The results of the isotherm test were thus inconclusive, only showing a higher capacity for the carbon reduced in air.

5.2.2 SILVER LOSS

A limiting factor in the number of times the carbon can be recycled, will be the amount of silver lost in every adsorption step. In Table 5.5 it can be seen that the amount of silver being lost in 24 h (in a 1L batch reactor, starting with 20 ppm free cyanide) is significant. After 24 hours, 15% of the silver had been lost. With the measurement technique used (atomic absorption spectrophotometry), only one significant figure could be attained.

An important factor in this loss is the residence time: longer contact time results in a larger loss.

5.2.3 HEAT TREATMENT OF VIRGIN CARBON

It was decided to test the effect of temperature alone on the adsorptive properties of virgin carbon. When the impregnation procedure was simulated without the addition of the silver salt, the carbon's capacity to adsorb free cyanide increased from 1mg/g of carbon to 3 mg/g of carbon. There were however, no visible signs of combustion. The heat treatment step therefore possibly altered the properties and/or structure of the virgin carbon. These results are show in Table 5.6. Since this capacity is still very low, this was not investigated further. Keep in mind that the capacity of the impregnated carbon reduced in nitrogen can be increased, by increasing the silver concentration in the impregnation step (Chapter 4.3).

5.3 REGENERATION

Regeneration of the carbon was not tested in this study. Schlettwein [45] reported good yields when recycling the impregnated carbon reduced in air for up to four times. An explanation of the rise in capacity after the first recycle lies in the fact that the carbon combusted, have a lower density and therefore higher surface area per gram.

The carbon reduced in a nitrogen atmosphere is robust and is expected to endure numerous cycles.

Table 5.1 Isotherm result for N_2 SIAC

CN^- solution	25 ppm	20 ppm	15 ppm	10 ppm	5 ppm
Ci (ppm)	24	20	15	10	5.5
Ce (ppm)	18.5	15	13.5	8.3	4
Qe (mg/g)	22	20	6	6.8	6

A = 6.1 n = 0.013

Table 5.2 Isotherm result for N_2 SIAC

CN^- solution	25 ppm	20 ppm	15 ppm	10 ppm	5 ppm
Ci (ppm)	26	21	15	9.6	4.7
Ce (ppm)	23	17.9	12	6.4	2.1
Qe (mg/g)	6	6.2	6	6.4	5.2

A = 5.2 n = 0.057

Table 5.3 Isotherm result for Air SIAC

CN^- solution	25 ppm	20 ppm	15 ppm	10 ppm	5 ppm
Ci (ppm)	19	15	10	7.2	3.5
Ce (ppm)	7.6	3.1	0.48	0.013	0.085
Qe (mg/g)	22.8	23.8	19.04	14.37	6.83

A = 17.8 **n = 0.132**

Table 5.4 Isotherm result for air SIAC

CN^- solution	25 ppm	20 ppm	15 ppm	10 ppm	5 ppm
Ci (ppm)	23	19	14	8.2	4
Ce (ppm)	16	8.3	7.4	3.5	0.9
Qe (mg/g)	35	54	33	24	16

A = 16.7 n = 0.355

Table 5.5 Silver loss in a batch configuration

time	Ag concentration (ppm)
0	0
5 s	1
50 min	2
24 h	3

Table 5.6 15 g virgin carbon in air atmosphere in furnace

Conditions :	temp	time (h)	atm.
	300	5	air

1 g of product in 1l 20 ppm KCN solution
24h test

Ci =	20
C =	17
Q =	**3**

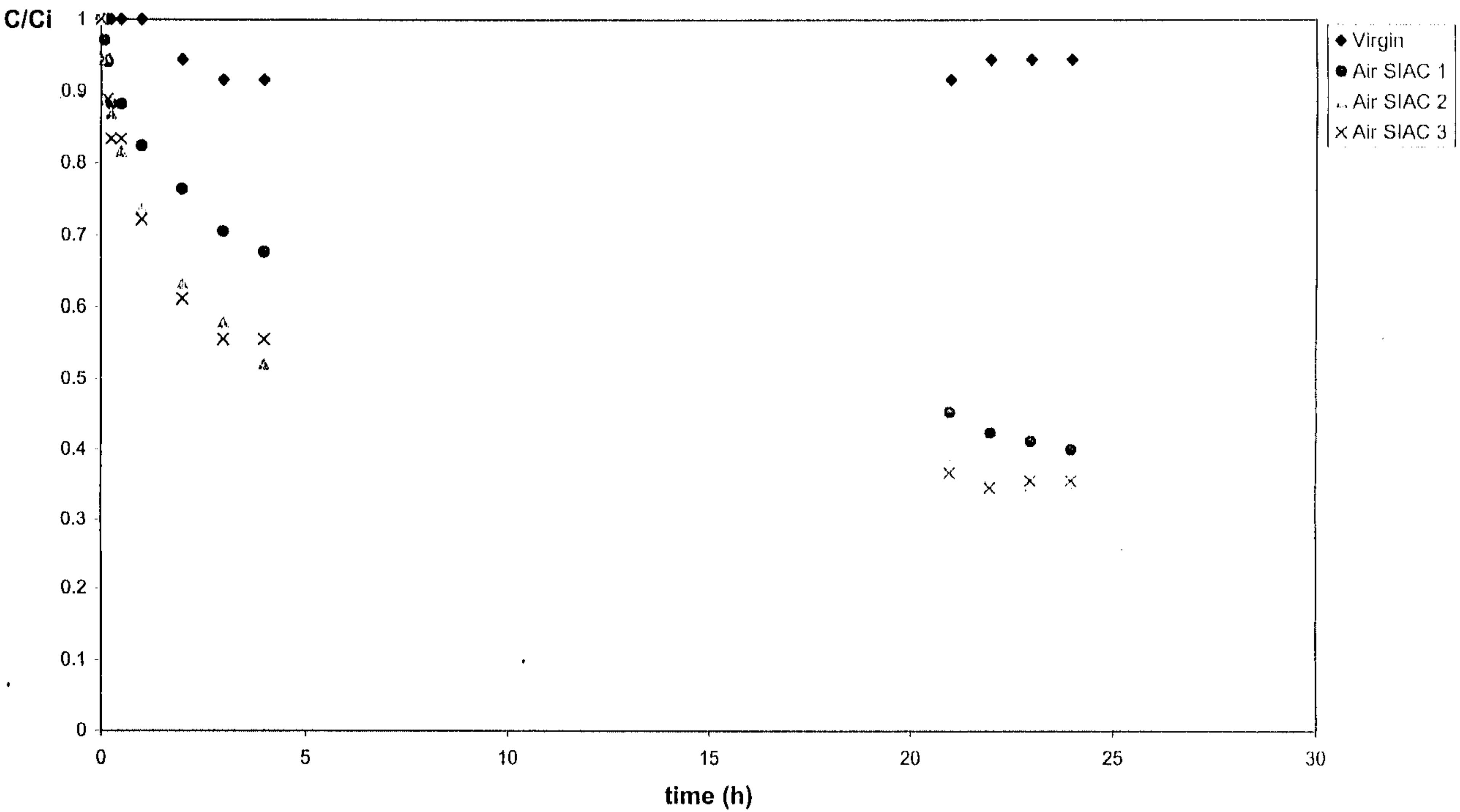


Figure 5.1 Performance of virgin carbon and air SIAC in a batch reactor
[Ci = 20 ppm, m_c = 1 g, stirring speed = 300 rpm]

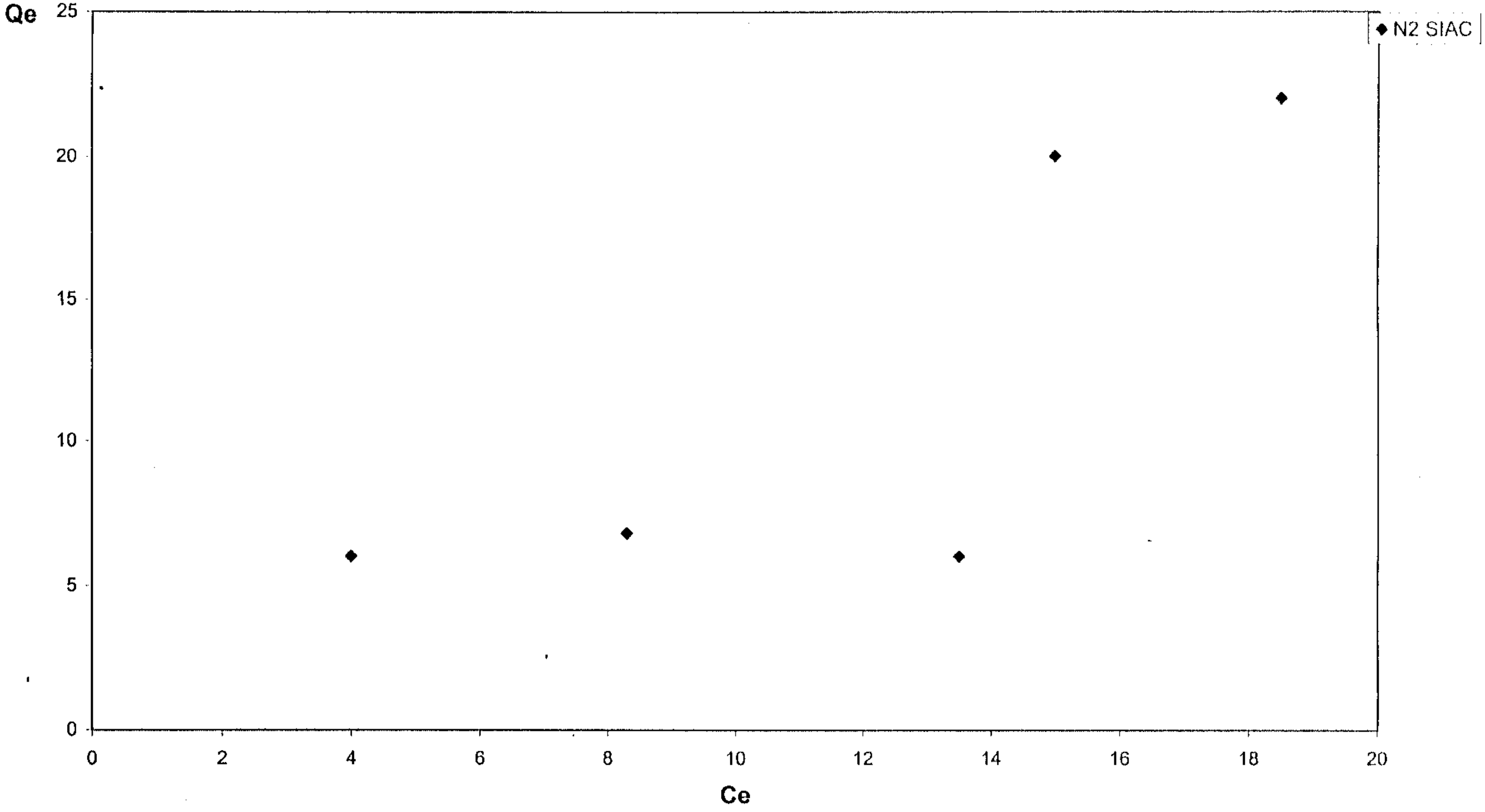


Figure 5.2 Isotherm plot of N2 SIAC
[0.25 g N_2 SIAC in each reactor, diffirent Ci]

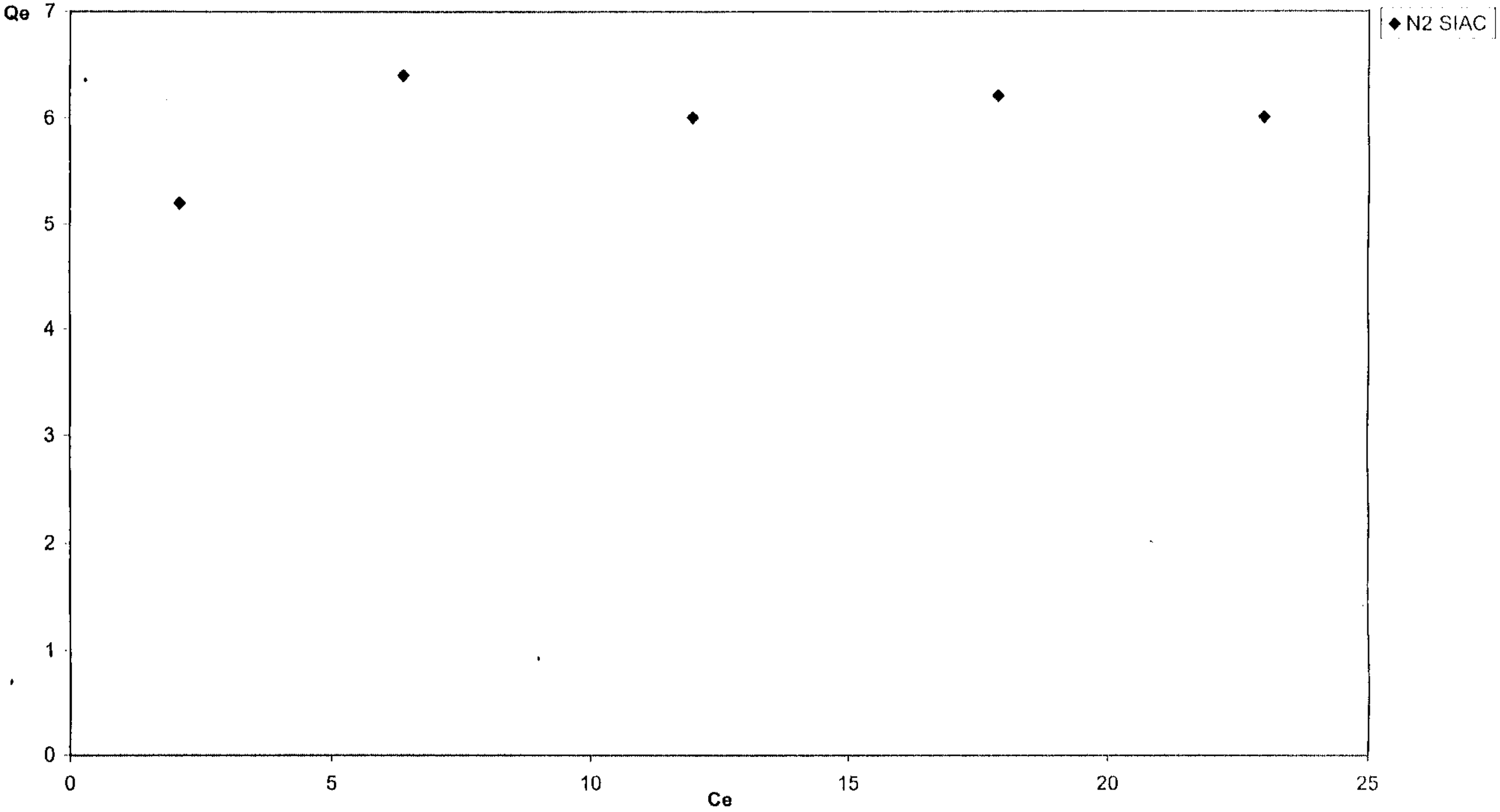


Figure 5.3 Isotherm plot of N_2 SAIC
[0,5g of N_2 carbon in each reactor, different C_i]

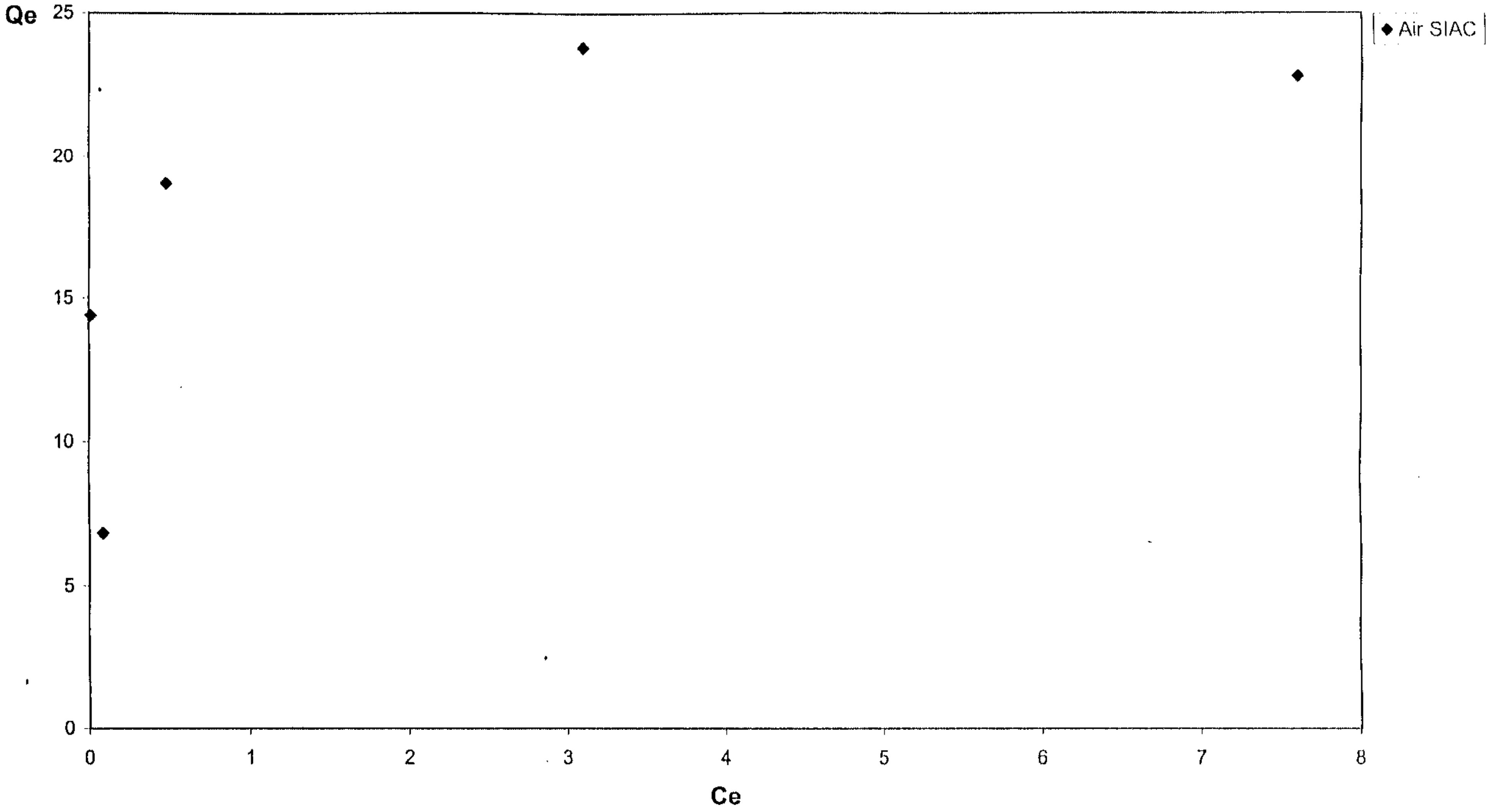


Figure 5.4 Isotherm plot of air SIAC
[0.5 g of air SIAC in each reactor, different Ci]

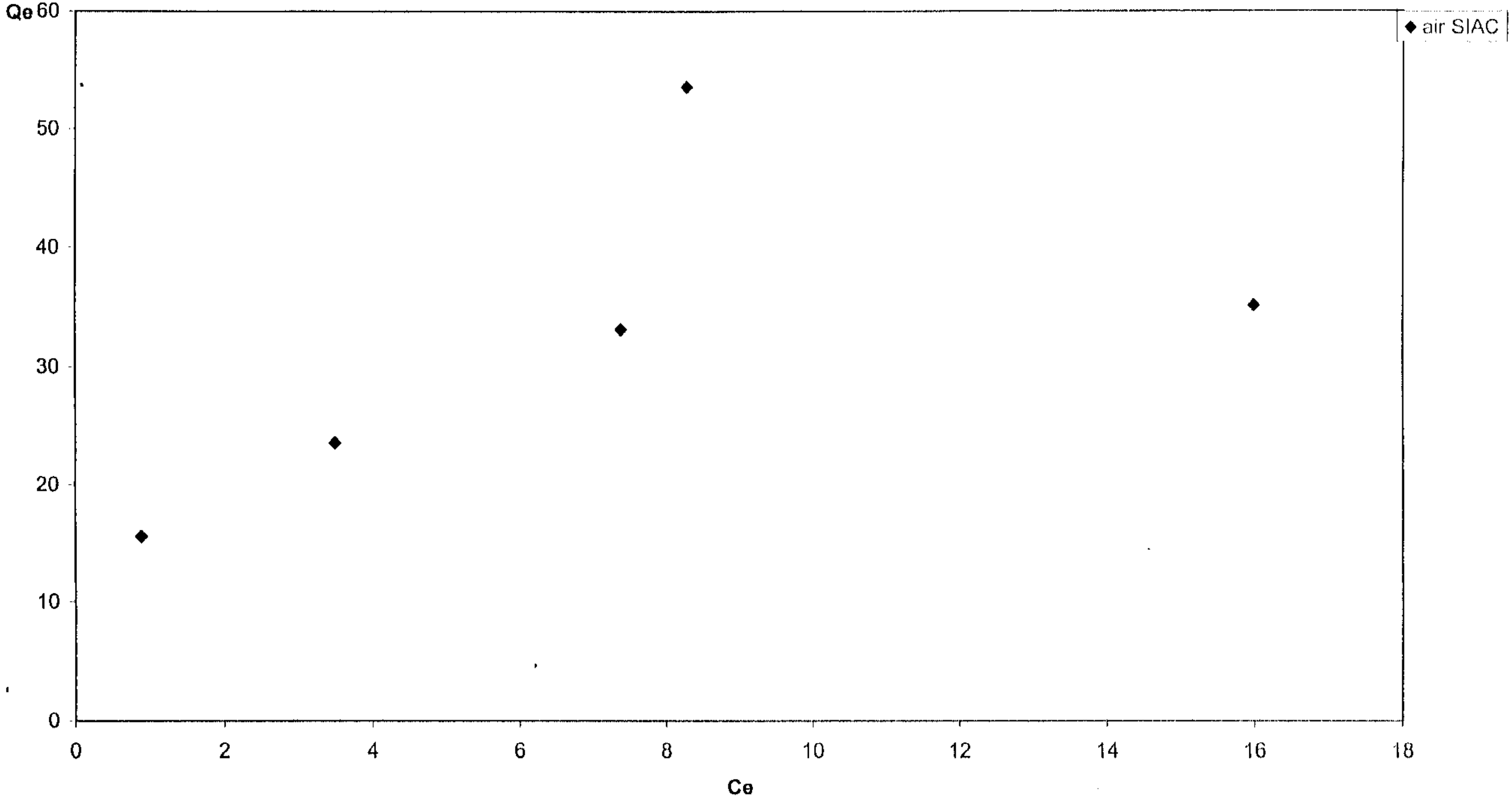


Figure 5.5 Isotherm plot of air SIAC
[0.25 g N_2 in each reactor, different C_i]

CHAPTER 6

ADSORPTION OF FREE CYANIDE IN A COLUMN CONFIGURATION

In a fixed bed either up-flow or gravitational flow can be used. In this study up-flow proved to yield erratic results and gravitational flow was therefore used throughout, except where otherwise stated. This gravitational operation excludes the possibility of fluidization.

The breakthrough curve was discussed in detail in Chapter 2. This is an important tool in analyzing the properties of a packed column. It gives an indication of the useful capacity of the column as well as the rate at which the reaction take place.

6.1 SMALL COLUMN EXPERIMENTS WITH AIR SIAC

From Figures 6.1 and 6.2 the problems with up-flow can be seen. The results are erratic and may be due to slight differences in the flow patterns or fluidization. This prevents accurate calculations of the reaction rate (k_f). The other results were obtained using gravitational flow and SIAC reduced in an air atmosphere (Figures 6.3, 6.4, 6.5 and 6.6).

Virgin washed carbon performed poorly in this column configuration and saturation was reached almost immediately, as can be seen in Figure 6.3. The SIAC yielded promising results, with an improvement visible when the carbon to cyanide ratio is increased. This effect is clear when comparing the breakthrough curves in Figures 6.4 and 6.5. The only parameter that is different in these two figures is the mass of carbon in the column – from 20g to 15g. When only 15g of impregnated carbon were used

(Figure 6.5), one can see that the breakthrough point and saturation is reached much quicker than when 20g of the same carbon (Figure 6.4) were used.

The effect of different particle sizes was investigated and, as could be expected, the smaller particles outperformed the larger particles (Figure 6.6). This is due to the larger surface area available for adsorption. However, the size of the particle limits the maximum flow rate, especially in cases where the air SIAC is used, since the breaking up of this brittle carbon blocks the column. Very fine particles, which will perform well in a batch configuration, will prevent proper flow in a column configuration.

In this column, the internal diameter (25 mm) is relatively small compared to the average particle diameter (an approximate factor of 14). A certain amount of disturbance from the column wall can therefore be expected. The sensitivity analysis was carried out with a column with a larger internal diameter (37 mm).

6.2 SENSITIVITY ANALYSIS OF OPERATING PARAMETERS

6.2.1 Standard Conditions

The following were chosen as the standard conditions for the sensitivity analysis:

Linear Velocity	12.5 cm/min
Bed Volume	125 ml
Feed concentration	20 ppm
Column diameter	37 mm
Gravitational flow	
N_2 SIAC	

6.2.2 Virgin Carbon

Under these conditions virgin carbon performed poorly. The saturation point was reached in a short time. Figure 6.7 represents this result. This is what is expected, if the virgin carbon's capacity in a batch configuration is taken into account (1-2 mg/g). Huge volumes of virgin carbon would be needed (and very low linear velocities) to remove significant amounts of free cyanide from the solution.

6.2.3 SIAC

6.2.3.1 Mass-transfer zone

As explained in Chapter 1, there are four simultaneous reactions that occur. There are thus four different mass transfer zones of different sizes. All of these might not be completed by the time the stream exit the column. Silver has been found in the exit stream. A larger bed of carbon is therefore proposed with possibly a layer of virgin carbon at the exit to prevent silver losses.

An example of the problems this can cause can be seen from the analysis of different bed volumes. The smallest bed reacts differently to the two larger beds (Figure 6.8). With the same linear velocity, initial concentration and measurements being done in bed volume units, one would have expected the results of all three tests to be similar. Instead, we have two similar results and one with a much quicker breakthrough. This could be due to the "reaction wave" of all four reactions not being completely formed by the time the effluent leaves the column in the case of the smallest bed volume. Although all four reactions occur simultaneously, there is a specific order to three main reactions (leaching, complex forming and adsorption of the complex). The bed needs to be high enough to accommodate at least one complete cycle of these reactions. In the two larger columns it seems as if all four reactions can be completed inside the length of the bed.

6.2.3.2 Results of Sensitivity Analysis

A summary of the results of a change in one parameter when all others are kept constant, on the overall rate of adsorption, is shown in Table 6.1.

- Bed Volume – As predicted by literature, an increase in the bed volume increases the performance. This effect can be seen by a comparison of the breakthrough curves in Figure 6.8. The effect is relatively small when the bed height (and height to diameter ratio) is above a certain value. This could be due to the complexity of the transfer mechanism. The solution can exit the column before all four reactions are complete or the adsorption waves properly formed. The breakthrough curves in these figures can only give an indication of a combined effect.

- An increase in the cyanide concentration in the feed is detrimental to the performance of the column (Figure 6.9). It has been reported [73] that the carbon to cyanide ratio is one of the most important factors in determining the capacity of the SIAC. This breakthrough curve implies that the solution passes through the column before all the reactions are completed.

- Lower linear velocities improve performance due to the longer reaction time available. However, a longer residence time can cause greater silver losses. The effect of an increase in linear velocity on the performance of the column operation can be seen in Figure 6.10. The fact that the column has a larger useful capacity when the flow rate is low, can clearly be see from these graphs – there is a longer period before the breakpoint and, thereafter, the concentration in the exit rises more slowly. This in turn shows that the apparent rate of diffusion is in fact lower when the flow rate is slower, but that the capacity is higher (the slope of the breakthrough curve after the breakpoint).

- As literature suggest [79], a larger column diameter with the same bed volume and linear flow rates, yield similar results to that of the smaller column. This is shown in Figure 6.11

6.2.4 Loading on the carbon and reaction rate

Table 6.2 lists the percentage of the cyanide that adsorbed onto the carbon to the total amount that entered the column. This value is calculated at two points: firstly where the cyanide in the exit stream equals 60% of that in the feed, and secondly at 70%. From this table it can be seen how adsorption differs with a change in a parameter, as explained in the above section. The differences are small, but that is due to tha fact that the total capacity of the carbon is relatively low (6mg/g).

In Table 6.1 the comparative k_f values for the different conditions are stated. This was calculated with the equations presented in Chapter 2. The reaction rate increases with an increase in velocity, and decrease when the bed volume or the column diameter increases. It must be noted that these k_f values are only an indication of the overall rate of the reactions that take place throughout the whole column.

6.3 MECHANISM

The proposed mechanism is the same as that for the batch configuration, but consideration must be given to the fact that a much more complex situation develops in the column configuration. This is due to the fact that the different reactions will have different rates of mass transfer. It is therefore possible to have a situation where some of the reactions have not been completed when the solution exits the column. This will lead to silver losses.

It should be noted that proposing a mechanism for the reactions is not the thrust of this thesis, but rather an understanding of the influence of different operating parameters on the functioning of the packed bed.

6.4 SCALE-UP OF COLUMN

More data points will be needed to make a recommendation on scaling the system to pilot plant level. It is recommended that the same column diameter be used, but a bed height and linear velocity equal to that in the proposed pilot column. This small scale test will reflect the same properties as that which would be present in the larger column. In the experiments discussed in this thesis, relatively small bed height was used for comparative reasons.

Table 6.1 Summary of kf values for the different conditions - sensitivity analysis of N_2 SIAC

LV	BV	Ci	Dc	kf	
12.5	125	20	37	0.04665	STANDARD
12.5	250	20	37	0.02287	
12.5	312.5	20	37	0.01974	
12.5	125	50	37	0.03982	
25	125	20	37	0.0861	
6	125	20	37	0.0237	
3.5	125	20	37	0.01111	
25	125	20	68	0.0263	

Table 6.2 Percentage of total CN^- feed that adsorbed onto the SIAC

Changing Condition	% of feed CN^- in effluent	
	60	70
Flow = 3.5 cm/min	68	60
Flow = 6 cm/min	67	58
Flow = 12.5 cm/min	63	55
Flow = 25 cm/min	60	52
Bed Volume = 250 ml	68	57
Bed Volume = 312.5 ml	67	56
Ci = 50 ppm	59	50
D_c = 68 mm/Flow = 25 cm/min	59	50

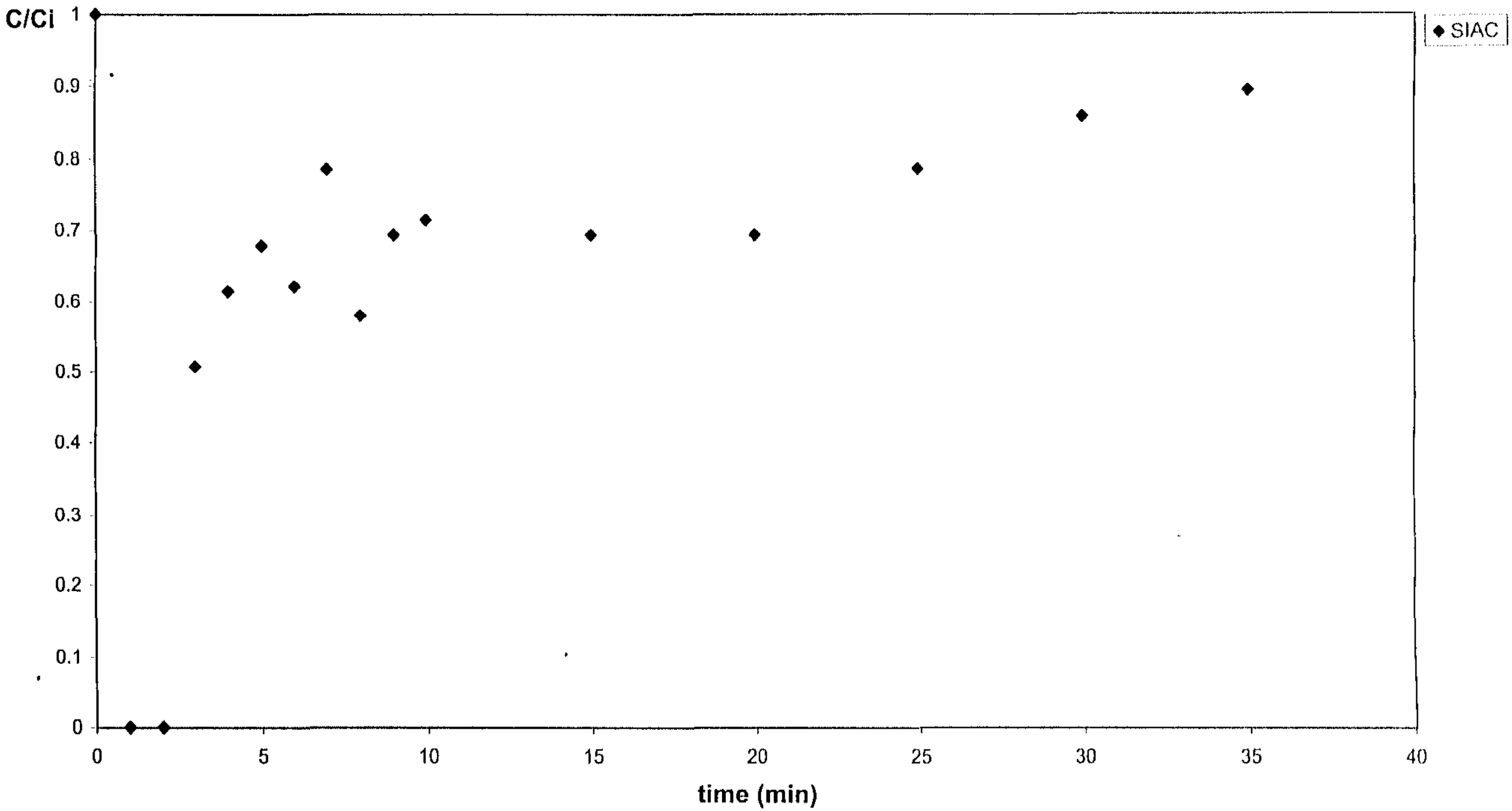


Figure 6.1 Breakthrou curve for up-flow in a small column
[Ci = 15 ppm, LV = 57 cm/ min, m_c = 15 g, D_c = 25 mm]

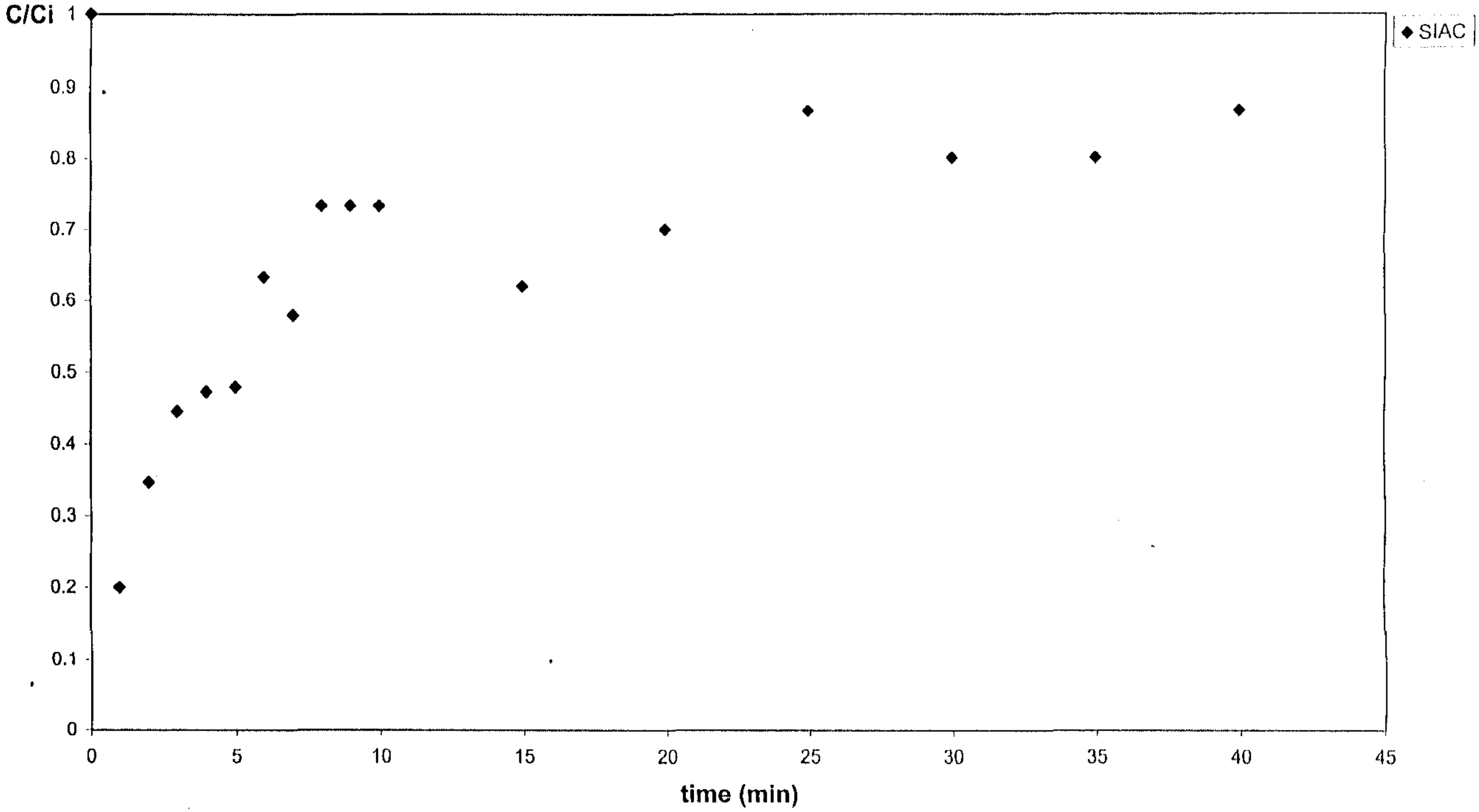


Figure 6.2 Breakthrough curve for up-flow in a small column
[Ci = 15 ppm, LV = 57 cm/min, m_c = 15 g, D_c = 25 mm]

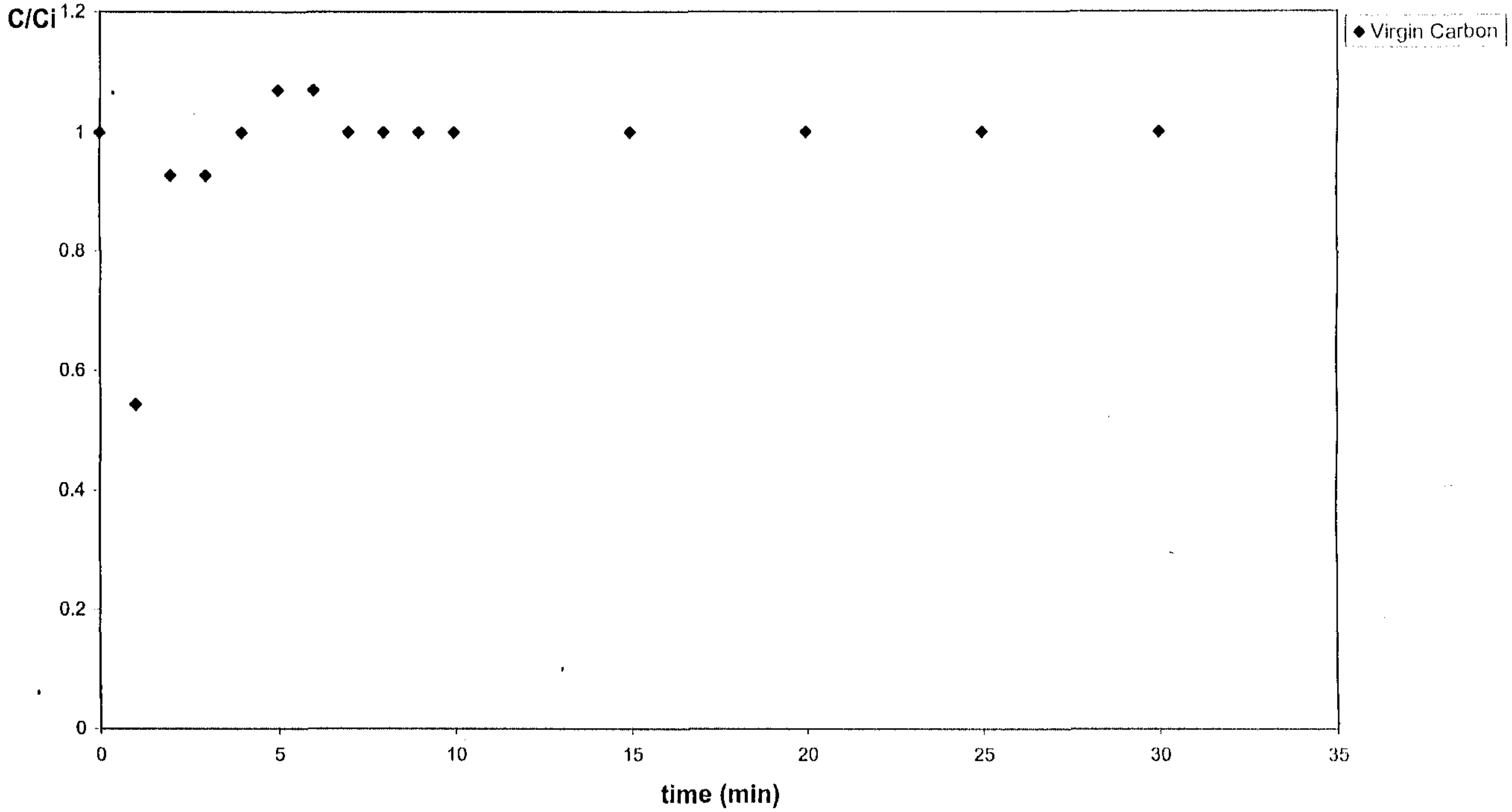


Figure 6.3 Breakthrough curve of virgin carbon in a small column
[LV = 42 cm/min, Ci =15 ppm, m_c = 20g]

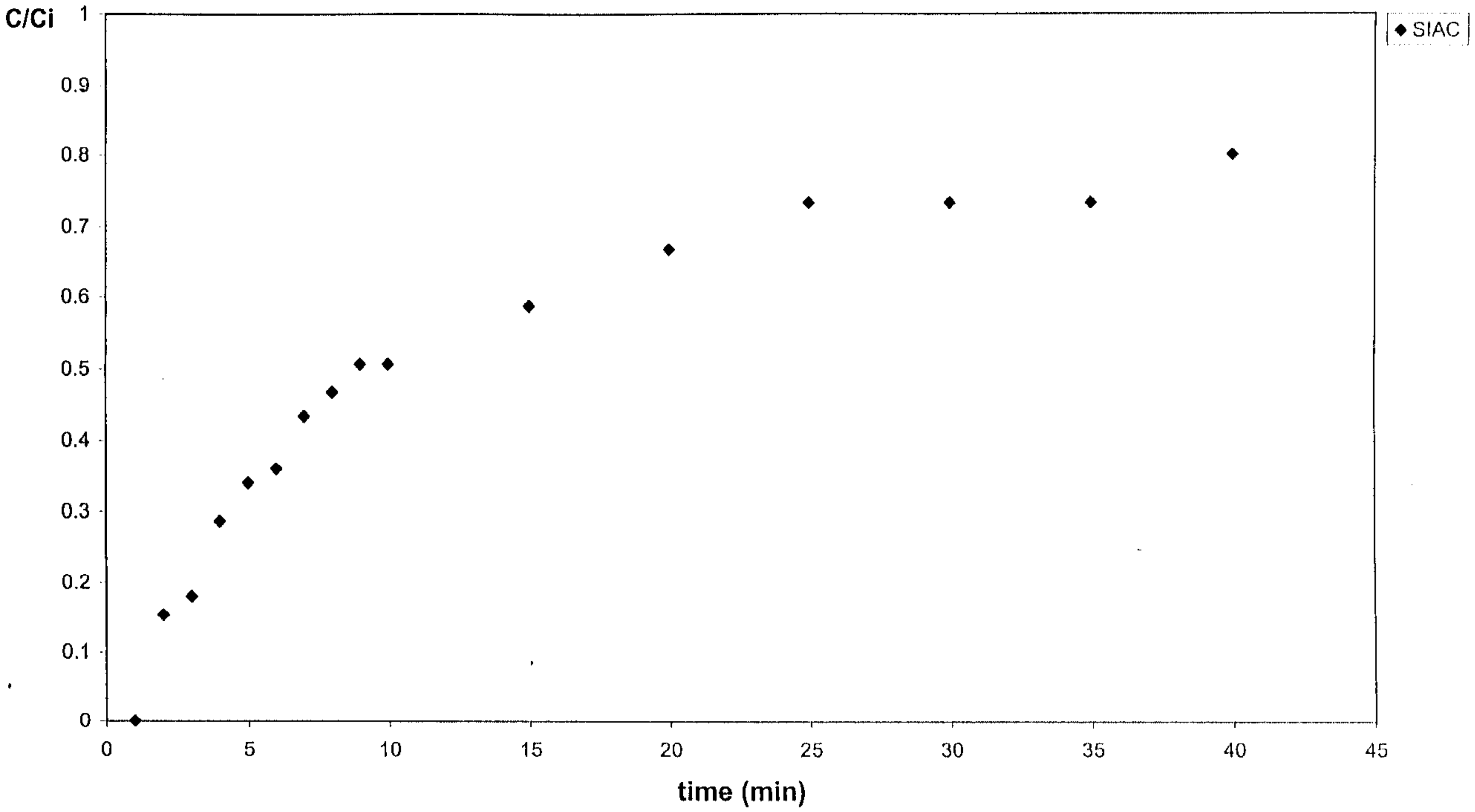


Figure 6.4 Breakthrough curve of 20 g SIAC (air)
[Ci = 15, LV = 42 cm/min, D_c = 25 mm]

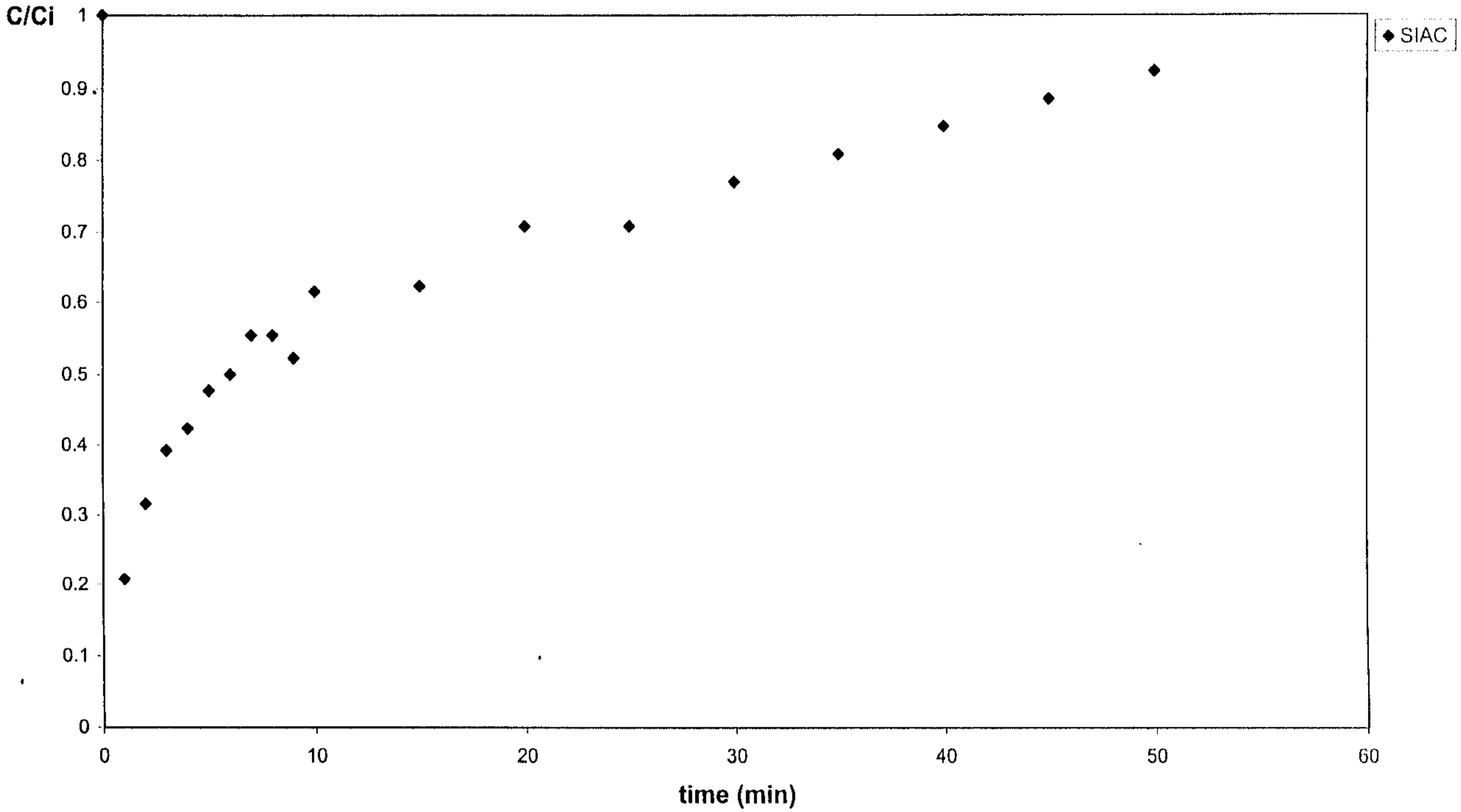


Figure 6.5 Breakthrough curve of 15 g of SIAC (air) in small column
[Ci = 15 ppm, LV = 42 cm/min, D_c = 25 mm]

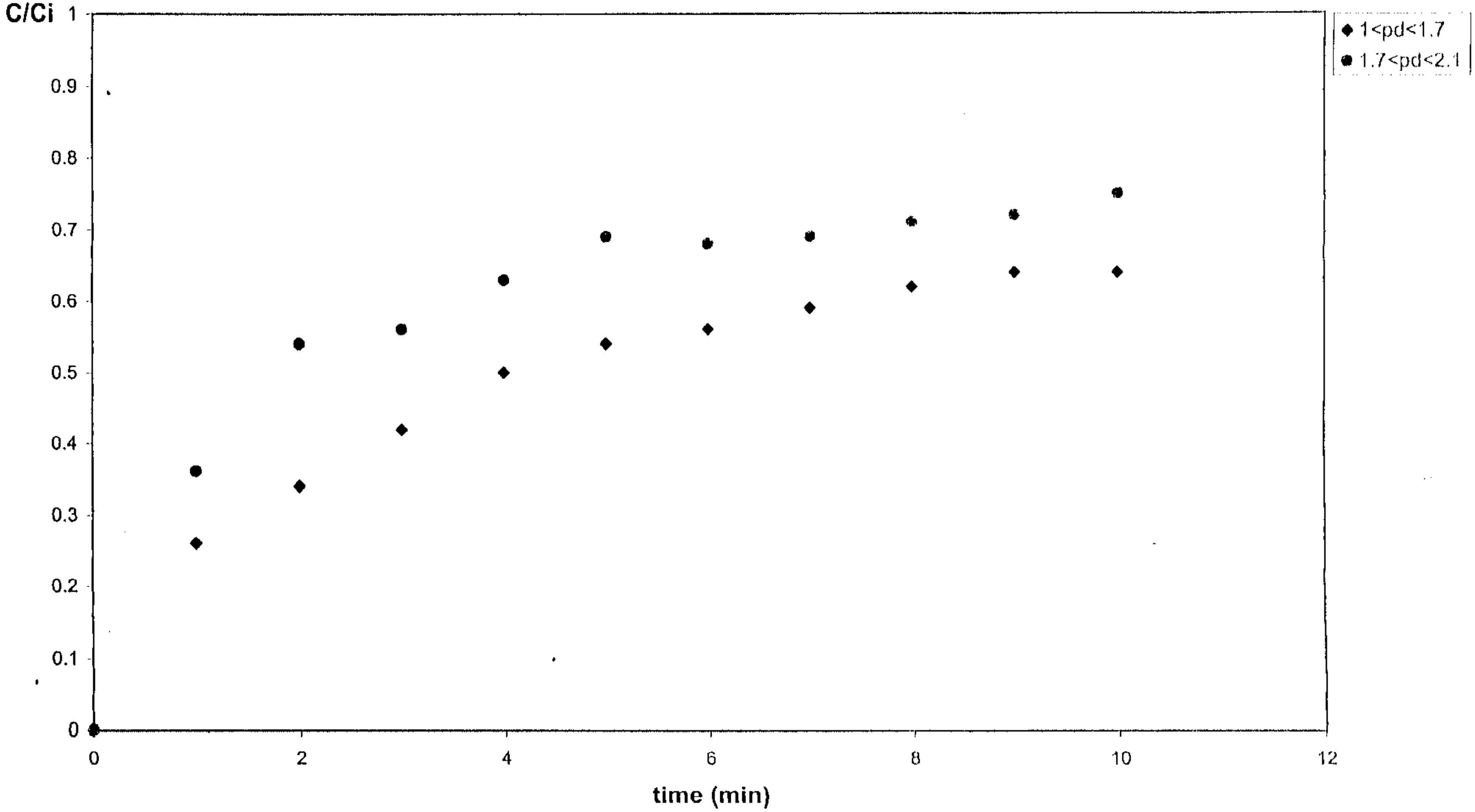


Figure 6.6 Breakthrou curves for two different particle sizes in a small column
[Ci = 10 ppm, LV = 57 cm/min, m_c = 7.5 g, D_c = 25 mm]

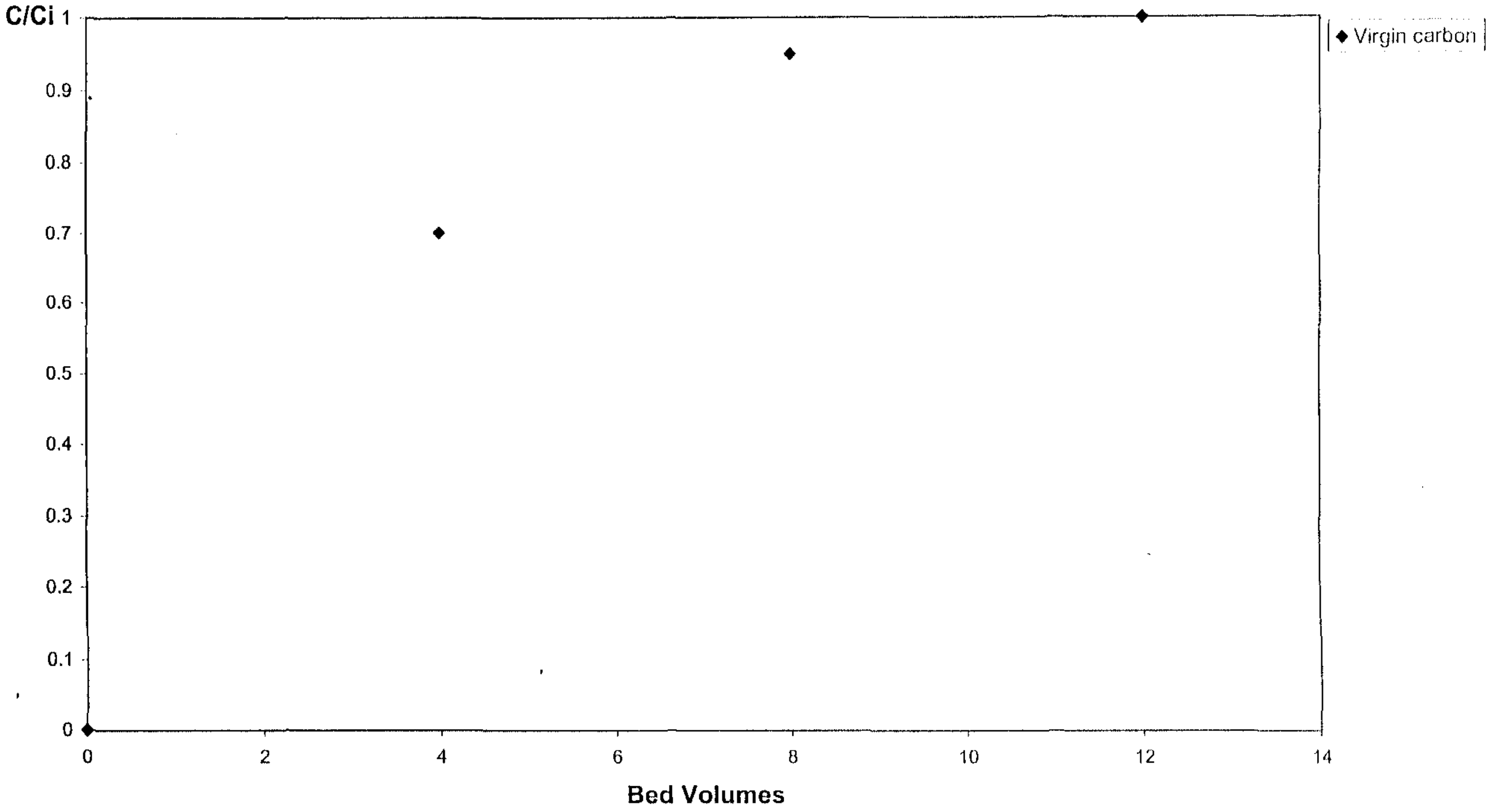


Figure 6.7 Breakthrough curve for virgin carbon
[Ci = 20 ppm, 1 bed volume = 125 ml, D_c =37 mm, LV = 12.5 cm/min]

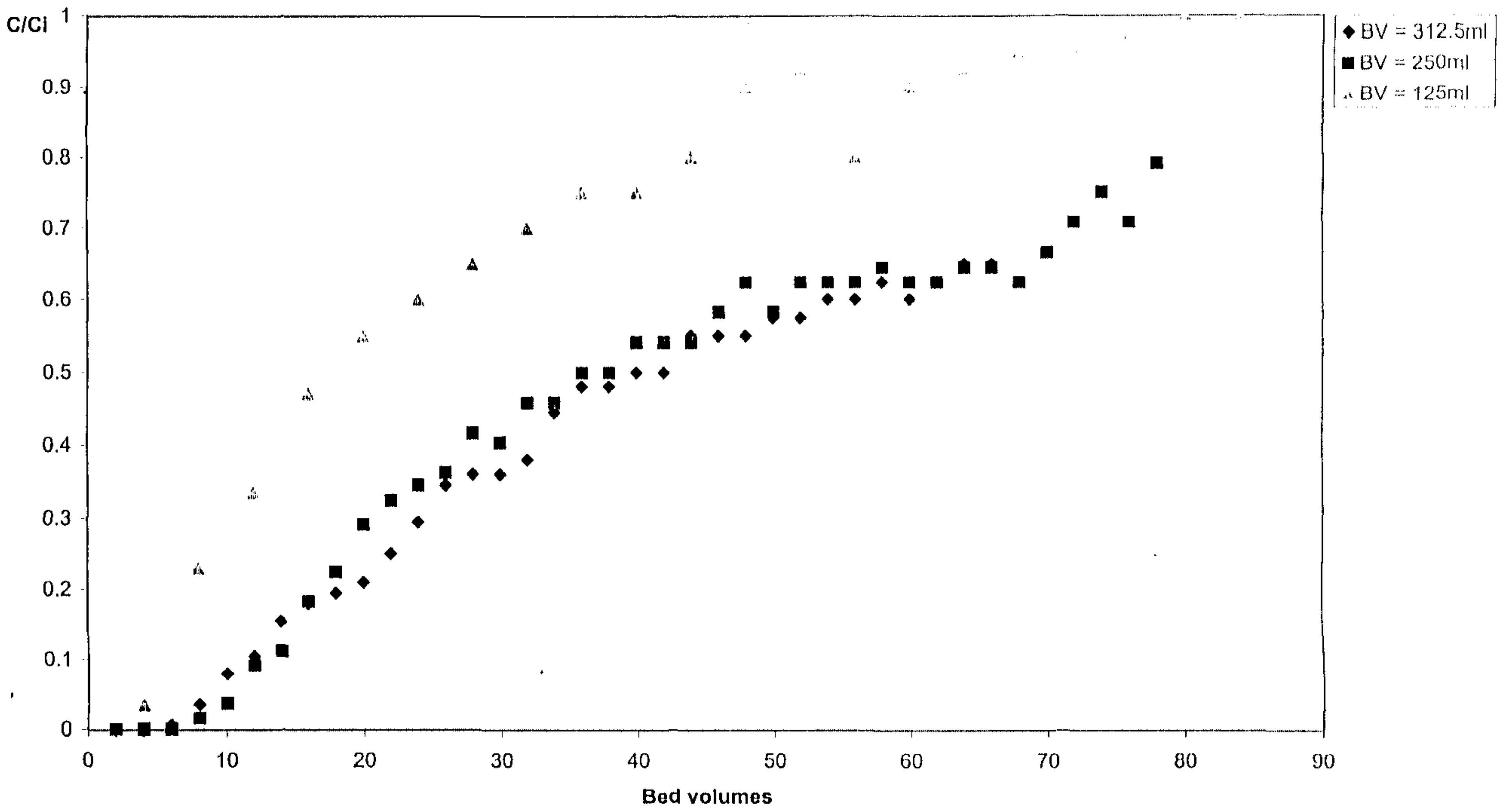


Figure 6.8 Effect of a change in Bed Volume
[Standard conditions with different size of bed]

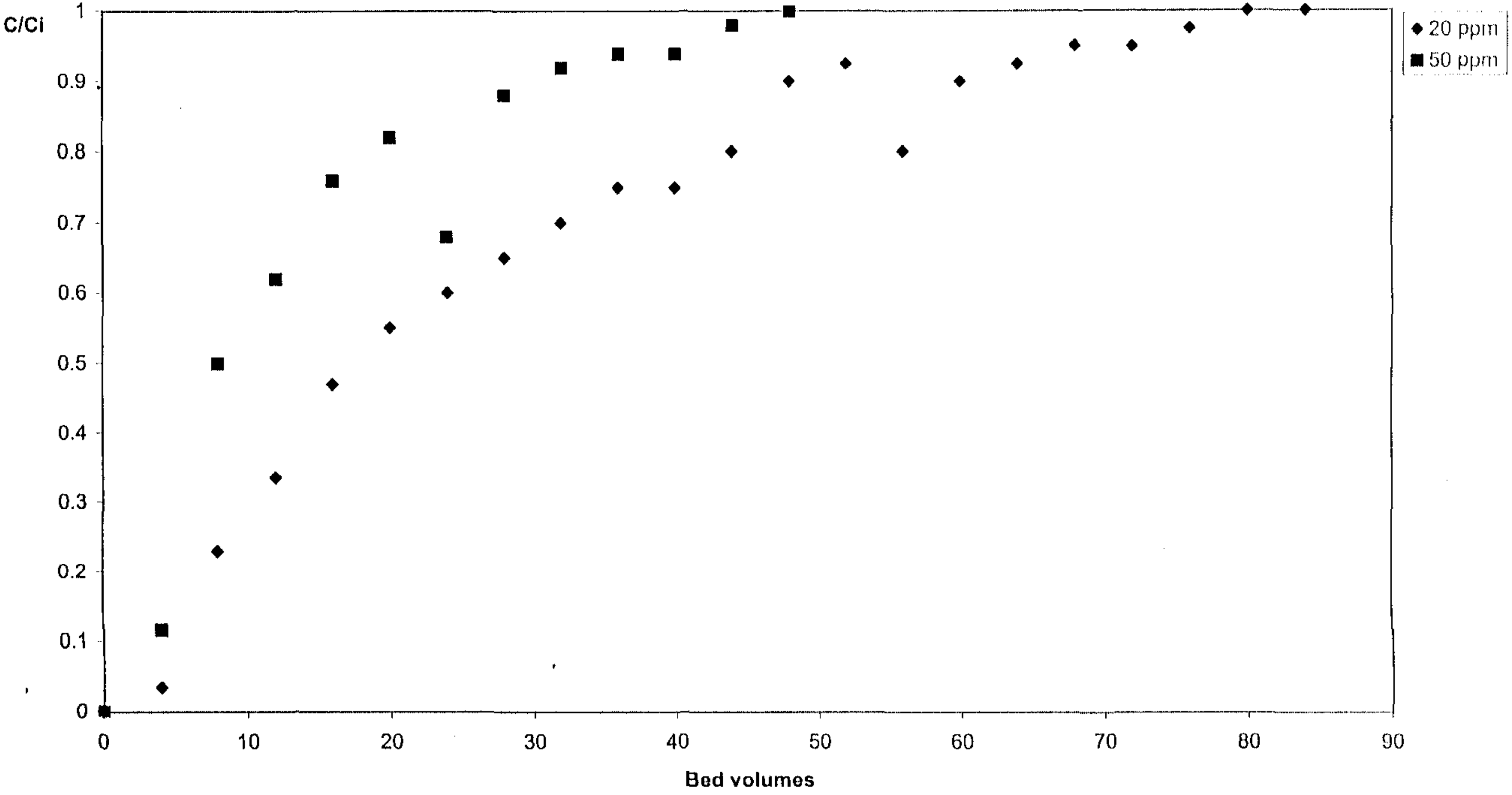


Figure 6.9 Effect of change in C_i
[Standard condition with different C_i]

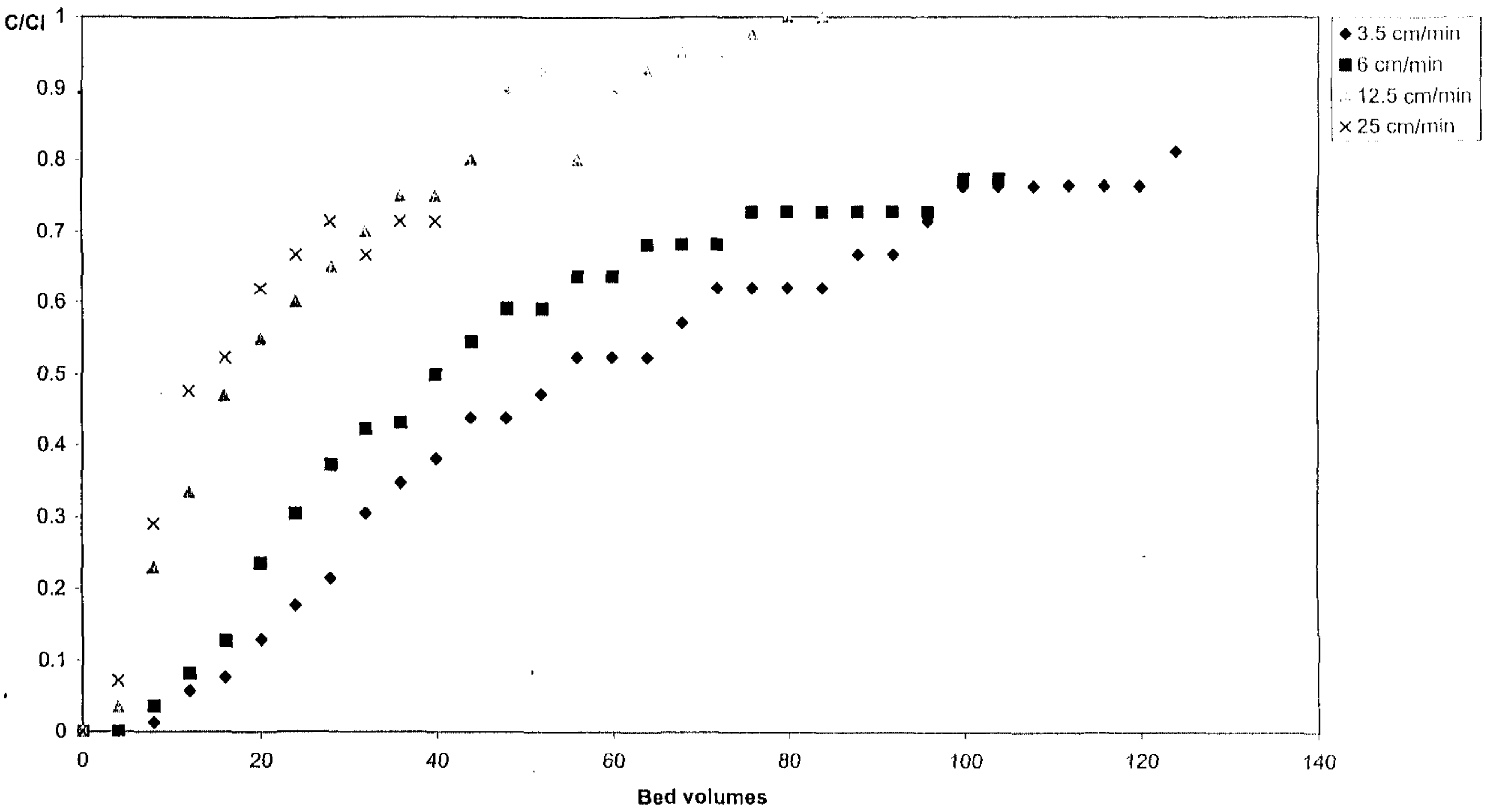


Figure 6.10 Effect of a change in linear velocity
[Standard conditions with different linear velocities]

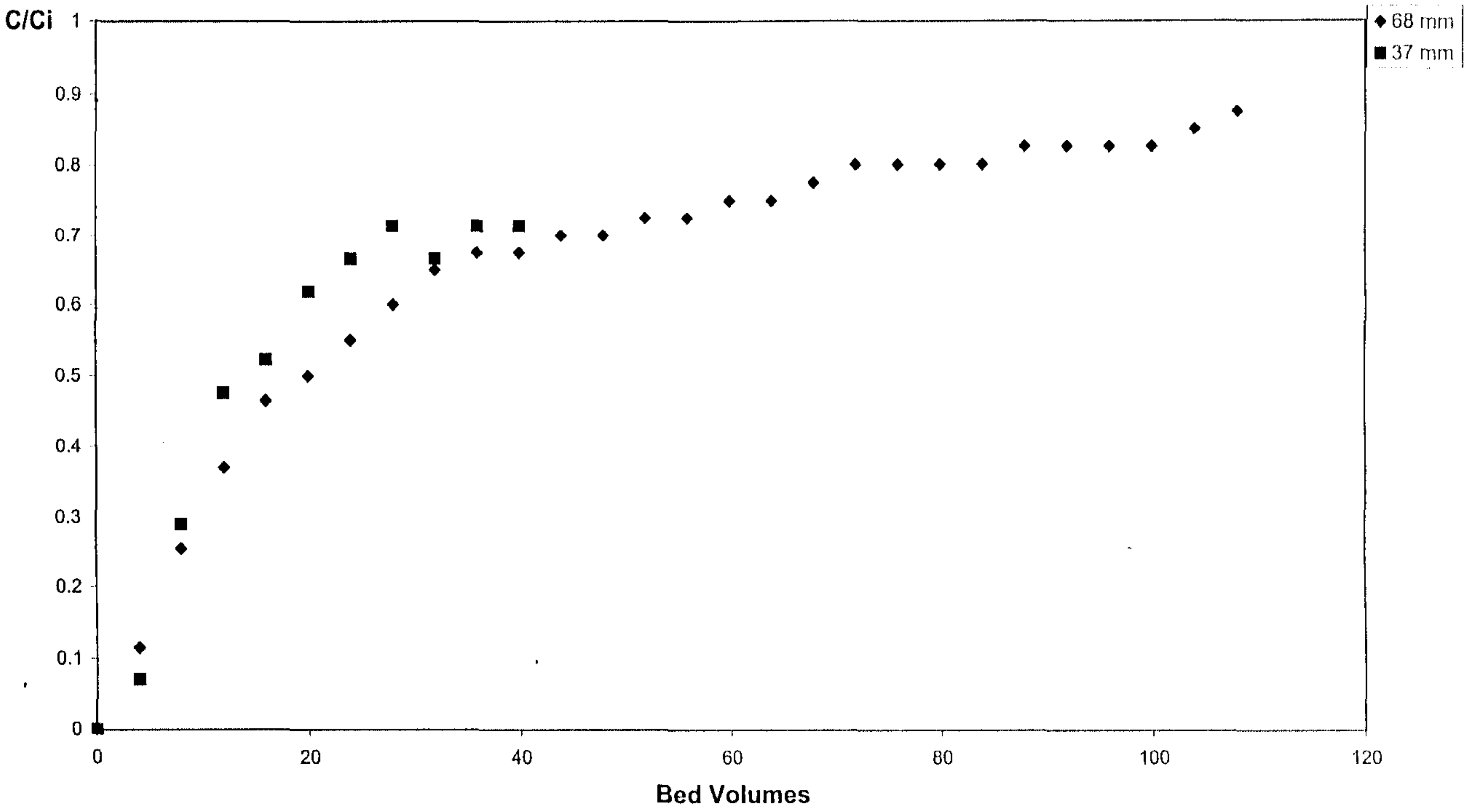


Figure 6.11 Effect of a change in column diameter
[Standard conditions with different column diameters]

CHAPTER 7

CONCLUSIONS

a) It was found that impregnating the activated carbon in an air atmosphere results in a large mass loss of carbon due to combustion. Losses of more than 50% are common and the resultant product is soft and brittle. This causes problems in transportation and the smaller particles also block the flow of solution in a packed bed. Executing the thermal step in a nitrogen atmosphere solves these problems, at the cost of a lower capacity. Increasing the silver loading on the carbon can increase the capacity.

b) Both types of silver impregnated activated carbon outperformed virgin activated carbon from both a kinetic and equilibrium point of view. This is the case in both the batch and column configurations. A Freundlich isotherm was tested, but the results were inconclusive.

c) Thermally treating virgin activated carbon in the same manner as in the impregnation procedure enhances the adsorptive properties, but not to the same level as the SIAC.

d) In the column configuration, the silver impregnated activated carbon proved to be successful in removing free cyanide from solution. The level of success are determined by the following factors:

  - The SIAC to cyanide ratio. Increasing the amount of SIAC available for adsorption will increase the performance of the packed bed.
  - Increasing the residence time of the solution in the packed bed has a positive effect on the performance.

- An increase in the free cyanide content of the feed solution has a large detrimental effect on the cyanide capacity of the packed bed.
- Increasing the column diameter while keeping other parameters constant (bed volume, linear velocity and feed concentration), have a negligible effect on the system. This fact can be used in the design of larger columns.

e) Silver losses have been found in both the batch and column configuration. This commences at a residence time of approximately 2 minutes, and longer residence times can cause greater silver losses.

RECOMMENDATIONS:

Although the SIAC in a packed bed is suitable for the removal of free cyanide from solution, the process is not highly effective due to the low cyanide capacity and SIAC production requirements. The capacity and rate of the reaction can be increased by further optimization of the carbon or increasing the silver loading on the carbon. However, this will increase the amounts of silver lost from the system. The process for manufacturing the SIAC is also energy intensive due to the high temperatures needed (500 °C). Removing the free cyanide from effluent is also only the first part of the process – the recovery from the carbon and/or the regeneration of the carbon will result in further expenses. After implementation, the effluent stream will also still require additional treatment with another method to meet the standards. The system investigated only reduce the cyanide levels to ppm levels. This is not sufficient. It is therefore proposed that another method, such as an ion exchange resin, be investigated for the clean-up of cyanide containing effluent streams. Also, further consideration should be given to the fact that cyanide is present in the effluent streams in other forms such as metal compounds. These compounds contribute to the total cyanide content of the streams since they can break down and release free cyanide. While SIAC remove free cyanide, the problem of these other compounds must still be investigated.

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NOMENCLATURE

A	parameter in Freundlich isotherm
C	concentration in solution (ppm)
C_i	initial concentration (ppm)
C_e	equilibrium concentration (ppm)
d_p	average particle diameter of activated carbon (mm)
H	bed height (m)
k_f	apparent rate constant of diffusion trough film (m/s)
LV	linear velocity (m/s)
m	mass of carbon (g)
n	exponential term in Freundlich isotherm
q_e	equilibrium loading (mg/g)
t	time (s)
V	volume (m^3)
ρ	density (kg/m^3)
ε	void fraction

APPENDIX A

TABULATION OF EXPERIMENTAL RESULTS

EXPERIMENT 1

1l 20ppm in batch reactor with 1g virgin carbon

Ci = 18

C	t(h)	C/Ci
18	0.0	1.0
18	0.1	1.0
18	0.2	1.0
18	0.3	1.0
19	0.5	1.1
19	1.0	1.1
19	2.0	1.1
18	3.0	1.0
18	4.0	1.0
17	21.0	0.9
16	22.0	0.9
17	23.0	0.9
17	24.0	0.9

EXPERIMENT 2

1l 20 ppm in reactor with 1g virgin C

Ci = 18

C	t(h)	C/Ci
18	0.0	1.0
18	0.1	1.0
18	0.2	1.0
18	0.3	1.0
18	0.5	1.0
18	1.0	1.0
17	2.0	0.9
16.5	3.0	0.9
16.5	4.0	0.9
16.5	21.0	0.9
17	22.0	0.9
17	23.0	0.9
17	24.0	0.9

EXPERIMENT 3

1l 20 ppm with 1g air SIAC in batch

Ci = 17

C	t(h)	C/Ci
17	0.0	0.9
16.5	0.1	0.9
16	0.2	0.9
15	0.3	0.8
15	0.5	0.8
14	1.0	0.8
13	2.0	0.7
12	3.0	0.7
11.5	4.0	0.6
7.7	21.0	0.4
7.2	22.0	0.4
7	23.0	0.4
6.8	24.0	0.4

EXPERIMENT 4

1l 20 ppm with 1g air SIAC in batch

Ci = 19

C	t(h)	C/Ci
19	0.0	1.0
18	0.1	1.0
17	0.2	0.9
16.5	0.3	0.9
15.5	0.5	0.9
14	1.0	0.8
12	2.0	0.7
11	3.0	0.6
9.9	4.0	0.6
7.2	21.0	0.4
6.8	22.0	0.4
6.6	23.0	0.4
6.5	24.0	0.4

EXPERIMENT 5

1 l 20 ppm with 1g air SIAC

Ci = 18

C	t(h)	C/Ci
18	0.0	1.0
17	0.1	0.9
16	0.2	0.9
15	0.3	0.8
15	0.5	0.8
13	1.0	0.7
11	2.0	0.6
10	3.0	0.6
10	4.0	0.6
6.6	21.0	0.4
6.21	22.0	0.3
6.4	23.0	0.4
6.4	24.0	0.4

EXPERIMENT 6

AIR SIAC ISOTHERM

0.5 g SIAC IN EVERY REACTOR WITH 1L SOLUTION
Ci FROM 5 TO 25

Ci	Ce	Qe
3.5	0.1	6.8
7.2	0.0	14.4
10	0.5	19.0
15	3.1	23.8
19	7.6	22.8

EXPERIMENT 7

AIR SIAC ISOTHERM

0.2g SIAC in each reactor with 1l solution
Ci between 5 and 25 ppm KCN
72 h

Ci	Ce	Qe
4	0.9	15.6
8.2	3.5	23.5
14	7.4	33.0
19	8.3	53.5
23	16.0	35.0

EXPERIMENT 8

N_2 SIAC ISOTHERM 1

0.5g SIAC in each reactor with 1l of solution
Ci between 5 and 25 ppm KCN
73 h

Ci	Ce	Qe
4.7	2.1	5.2
9.6	6.4	6.4
15	12.0	6.0
21	17.9	6.2
26	23.0	6.0

EXPERIMENT 9

N_2 SIAC ISOTHERM

0.25g SIAC in batch reactors with 1l solutions
Ci between 5 and 25 ppm KCN
48 h

Ci	Ce	Qe
5.5	4.0	6.0
10	8.3	6.8
15	13.5	6.0
20	15.0	20.0
24	18.5	22.0

EXPERIMENT 10

Optimisation of Nitrogen atmosphere condition in impregnation

Ci	C	time(h)	temp.(C)	capacity(mg/g)
14	12	5	250	2
14	12	0.5	300	2
20	17	2	500	3
13	10.5	0.5	500	2.5
19.5	13.5	4	700	6
20	**14**	**2**	**700**	**6**

EXPERIMENT 11

SMALL COLUMN WITH VIRGIN CARBON
Ci = 14
SPEED = (2) 0.0104 m^3/h 41.7 cm/min
MASS = 20g
gravitational flow

C	t(min)	C/Ci
14	0	1.0
7.6	1	0.5
13	2	0.9
13	3	0.9
14	4	1.0
15	5	1.1
15	6	1.1
14	7	1.0
14	8	1.0
14	9	1.0
14	10	1.0
14	15	1.0
14	20	1.0
14	25	1.0
14	30	1.0

EXPERIMENT 12

small column with air SIAC

Ci = 15

mass = 20g

speed = (2) 0.0104 m^3/h 41.7 cm/min

gravitational flow

C	t(min)	C/Ci
	1	0.0
2.3	2	0.2
2.7	3	0.2
4.3	4	0.3
5.1	5	0.3
5.4	6	0.4
6.5	7	0.4
7	8	0.5
7.6	9	0.5
7.6	10	0.5
8.8	15	0.6
10	20	0.7
11	25	0.7
11	30	0.7
11	35	0.7
12	40	0.8

EXPERIMENT 13

small column with air SIAC
Ci = 13
mass = 15g
speed = (2) 0.0104 m^3/h 41.7 cm/min
grivitational flow

C	t(min)	C/Ci
13	0	1.0
2.7	1	0.2
4.1	2	0.3
5.1	3	0.4
5.5	4	0.4
6.2	5	0.5
6.5	6	0.5
7.2	7	0.6
7.2	8	0.6
6.8	9	0.5
8	10	0.6
8.1	15	0.6
9.2	20	0.7
9.2	25	0.7
10	30	0.8
10.5	35	0.8
11	40	0.8
11.5	45	0.9
12	50	0.9

EXPERIMENT 14

small column with air SIAC
Ci = 14
mass = 15g
flow = (3) 0.0141 m^3/h 56.6 cm/min
up flow

C	t(min)	SIAC
14	0	1.0
	1	0.0
	2	0.0
7.1	3	0.5
8.6	4	0.6
9.5	5	0.7
8.7	6	0.6
11	7	0.8
8.1	8	0.6
9.7	9	0.7
10	10	0.7
9.7	15	0.7
9.7	20	0.7
11	25	0.8
12	30	0.9
12.5	35	0.9

EXPERIMENT 15

small column with air SIAC
Ci = 15
mass = 15g

speed = 0.0141 m^3/h
L/D = 12.5/2.3
flow = up-flow

C	t(min)	SIAC
15	0	1.0
3	1	0.2
5.2	2	0.3
6.7	3	0.4
7.1	4	0.5
7.2	5	0.5
9.5	6	0.6
8.7	7	0.6
11	8	0.7
11	9	0.7
11	10	0.7
9.3	15	0.6
10.5	20	0.7
13	25	0.9
12	30	0.8
12	35	0.8
13	40	0.9

EXPERIMENT 16

Mini column test in small column with 1mm<pd<1.7mm SIAC particles

Ci = 10

mass = 6.73g

L/D = 3

speed =(3) 0.0141 m^3/h 56.6 cm/min

gravitational flow

C	t(min)	1<pd<1.7
	0	0.0
2.6	1	0.3
3.4	2	0.3
4.2	3	0.4
5	4	0.5
5.4	5	0.5
5.6	6	0.6
5.9	7	0.6
6.2	8	0.6
6.4	9	0.6
6.4	10	0.6

EXPERIMENT 17

Mini column test in small column with SIAC
Ci = 10
mass = 8.55g
speed =(3) 0.0141 m^3/h 56.6 cm/min
L/D = 3
gravitational flow

C	t(min)	C/Ci
10	0	1.0
3.6	1	0.4
5.4	2	0.5
5.6	3	0.6
6.3	4	0.6
6.9	5	0.7
6.8	6	0.7
6.9	7	0.7
7.1	8	0.7
7.2	9	0.7
7.5	10	0.8

EXPERIMENT 18

linear velocity = 3.5 cm/min
std cond.
sample size = 4 BV
Ci = 21

effluent []	Bed Volume	C/Ci
0	0	0.0
0	4	0.0
0.27	8	0.0
1.2	12	0.1
1.6	16	0.1
2.7	20	0.1
3.7	24	0.2
4.5	28	0.2
6.4	32	0.3
7.3	36	0.3
8	40	0.4
9.2	44	0.4
9.2	48	0.4
9.9	52	0.5
11	56	0.5
11	60	0.5
11	64	0.5
12	68	0.6
13	72	0.6
13	76	0.6
13	80	0.6
13	84	0.6
14	88	0.7
14	92	0.7
15	96	0.7
16	100	0.8
16	104	0.8
16	108	0.8
16	112	0.8
16	116	0.8
16	120	0.8
17	124	0.8

EXPERIMENT 19

linear velocity = 6 cm/min
std. Cond.
sample size = 4 BV
Ci = 22

C	BV	C/Ci
0	0	0.0
0	4	0.0
0.8	8	0.0
1.8	12	0.1
2.8	16	0.1
5.2	20	0.2
6.7	24	0.3
8.2	28	0.4
9.3	32	0.4
9.5	36	0.4
11	40	0.5
12	44	0.5
13	48	0.6
13	52	0.6
14	56	0.6
14	60	0.6
15	64	0.7
15	68	0.7
15	72	0.7
16	76	0.7
16	80	0.7
16	84	0.7
16	88	0.7
16	92	0.7
16	96	0.7
17	100	0.8
17	104	0.8

EXPERIMENT 20

linear velocity = 12.5 cm/min
std. Cond.
sample size = 4 BV
Ci = 20

C	BV	C/Ci
0	0	0.0
0.7	4	0.0
4.6	8	0.2
6.7	12	0.3
9.4	16	0.5
11	20	0.6
12	24	0.6
13	28	0.7
14	32	0.7
15	36	0.8
15	40	0.8
16	44	0.8
18	48	0.9
18.5	52	0.9
16	56	0.8
18	60	0.9
18.5	64	0.9
19	68	1.0
19	72	1.0
19.5	76	1.0
20	80	1.0
20	84	1.0

EXPERIMENT 21

linear velocity = 25 cm/min
std. Cond.
sample size = 4 BV
Ci = 21

C	Bed Volume	C/Ci
0	0	0.0
1.5	4	0.1
6.1	8	0.3
10	12	0.5
11	16	0.5
13	20	0.6
14	24	0.7
15	28	0.7
14	32	0.7
15	36	0.7
15	40	0.7

EXPERIMENT 22

bed volume = 250 ml
std. Cond
sample size = 2 BV
Ci= 24

C	BV	C/Ci
0	0	0.0
0	2	0.0
0.026	4	0.0
0.037	6	0.0
0.39	8	0.0
0.9	10	0.0
2.2	12	0.1
2.7	14	0.1
4.4	16	0.2
5.4	18	0.2
7	20	0.3
7.8	22	0.3
8.3	24	0.3
8.7	26	0.4
10	28	0.4
9.7	30	0.4
11	32	0.5
11	34	0.5
12	36	0.5
12	38	0.5
13	40	0.5
13	42	0.5
13	44	0.5
14	46	0.6
15	48	0.6
14	50	0.6
15	52	0.6
15	54	0.6
15	56	0.6
15.5	58	0.6
15	60	0.6
15	62	0.6
15.5	64	0.6
15.5	66	0.6
15	68	0.6
16	70	0.7
17	72	0.7
18	74	0.8
17	76	0.7
19	78	0.8

EXPERIMENT 23

bed volume = 312.5 ml
std. Cond
sample size = 2 BV
Ci = *20*

C	BV	C/Ci
0	0	0.0
0	2	0.0
0	4	0.0
0.12	6	0.0
0.71	8	0.0
1.6	10	0.1
2.1	12	0.1
3.1	14	0.2
3.6	16	0.2
3.9	18	0.2
4.2	20	0.2
5	22	0.3
5.9	24	0.3
6.9	26	0.3
7.2	28	0.4
7.2	30	0.4
7.6	32	0.4
8.9	34	0.4
9.6	36	0.5
9.6	38	0.5
10	40	0.5
10	42	0.5
11	44	0.6
11	46	0.6
11	48	0.6
11.5	50	0.6
11.5	52	0.6
12	54	0.6
12	56	0.6
12.5	58	0.6
12	60	0.6
12.5	62	0.6
13	64	0.7
13	66	0.7

EXPERIMENT 24

initial conc. = 50 ppm KCN
std. Cond.
sample size = 4 BV
Ci = *50*

C	sample	C/Ci
0	0	0.0
5.8	4	0.1
25	8	0.5
31	12	0.6
38	16	0.8
41	20	0.8
34	24	0.7
44	28	0.9
46	32	0.9
47	36	0.9
47	40	0.9
49	44	1.0
50	48	1.0

EXPERIMENT 25

virgin carbon
std. Cond
sample size = 4 BV
Ci = 20

C	BV	C/Ci
0	0	0.0
14	4	0.7
19	8	1.0
20	12	1.0

EXPERIMENT 26

column diameter = 68mm
bed volume = 125 ml
linear velocity = 25 cm/min
sample size = 4 BV
Ci = 20

C	BV	C/Ci
0	0	0.0
2.3	4	0.1
5.1	8	0.3
7.4	12	0.4
9.3	16	0.5
10	20	0.5
11	24	0.6
12	28	0.6
13	32	0.7
13.5	36	0.7
13.5	40	0.7
14	44	0.7
14	48	0.7
14.5	52	0.7
14.5	56	0.7
15	60	0.8
15	64	0.8
15.5	68	0.8
16	72	0.8
16	76	0.8
16	80	0.8
16	84	0.8
16.5	88	0.8
16.5	92	0.8
16.5	96	0.8
16.5	100	0.8
17	104	0.9
17.5	108	0.9