The adsorption of gold from iodide solutions

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DECLARATION

I hereby certify that this dissertation is my own original work, except where specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has been submitted at any other Technikon.

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ABSTRACT

With the increasing awareness of preserving the environment, the need for other lixiviants in leaching processes has escalated. The investigation for lixiviants, especially for gold, has entailed mostly the halogen group. From halogens, iodine forms the most stable gold complex. The aim of this study was to investigate the adsorption characteristics of gold-iodide onto a coconut shell based activated carbon.

In the first part of this study, the factors influencing the adsorption kinetics and equilibrium were investigated. Mixing experiments and interruption tests indicated clearly that the principal adsorption mechanism is by first order film diffusion. When the initial gold concentration was changed, the adsorption kinetics and equilibrium decrease with an increase in gold concentration. This is due to the shielding effect by the adsorbed gold as it is partly reduced on the carbon surface. The concentration of iodide increased the adsorption kinetics and equilibrium. The increase in concentration of iodine leads to an increase in concentration of the principal oxidising agent, tri-iodide, thereby decreasing the adsorption parameters as the gold gets re-dissolved from the carbon surface. Furthermore, iodine and trio-iodide adsorbs competitively, thereby decreasing the rate of adsorption of the gold complex. This is further iterated by experiments where the carbon was pre-treated with a iodine/iodide solution.

In acidic solutions, none, or a minimal amount of the gold is reduced on the carbon surface, adsorption is only in the complex form, while in a alkaline solution, the gold is partly adsorbed and partly reduced.

In the second section, the adsorption is approached from a basic electrochemical perspective. Here, depending on the pH of the solution, it is shown that the potential of the solution dictates the species of iodine and gold-iodide complex in solution, it affects the adsorption characteristics of the activated carbon.

OPSOMMING

Met die toenemende bewustheid in die bewaring van die omgewing, het die behoefte vir alternatiewe loogmiddels aansienlik vergroot. Die ondersoek na loogmiddels, veral vir goud, het hoofsaaklik die halogeengroep behels. Van die halogene, vorm jodium die stabielste goudkompleks. Dit was die doel van hierdie studie om die adsorpsie karakteristieke van goudjodied op kokosneutdop-gebaseerde geaktiveerde koolstof te ondersoek.

In die eerste gedeelte van die studie is die faktore wat die adsorpsie kinetika en ewewig beïnvloed, ondersoek. Meng eksperimente en onderbrekingstoetse het duidelik aangetoon dat die hoofadsorpsie meganisme 'n eerste-orde film diffusie is. In die geval waar die begin konsentrasie van goud verander is, het die adsorpsie kinetika en ewewig verminder met 'n toename in goudkonsentrasie. Dit is as gevolg van die afskermende effek van die geadsorbeerde goud, aangesien dit gedeeltelik gereduseer word op die koolstof oppervlakte. Die konsentrasie van jodied verhoog die adsorpsie kinetika en ewewig. Die verhoging in konsentrasie van jodium, lei tot 'n verhoging in die konsentrasie van die hoofoksideermiddel, naamlik, trijodied. Dit verlaag die adsorpsie parameters deurdat die goud heroplos vanaf die koolstof oppervlakte. Verder is gevind dat die jodium en trijodied kompeterend adsorbeer. Dit lei tot 'n verlaging in die snelheid van adsorpsie van die goud kompleks. Dit is verder ondersteun deur eksperimente waar die koolstof vooraf behandel is met 'n jodium/jodied oplossing.

In suur media word geen of baie min van die goud gereduseer op die koolstof oppervlakte, dit wil sê, adsorpsie is slegs in die komplekstoestand, terwyl in 'n alkaliese oplossing die goud slegs gedeeltelik geadsorbeer en gereduseer word. Dit affekteer die adsorpsie ewewigte.

In die tweede deel, word die adsorpsie benader vanuit 'n elektrochemiese perspektief. Hier word dit aangetoon dat, afhangende van die pH van die medium, die potensiaal van die oplossing die spesies van jodium en goudjodied kompleks in oplossing dikteer en die adsorpsie karakteristieke van die geaktiveerde koolstof affekteer.

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CHAPTER 1

INTRODUCTION

1.1 THE HISTORY OF GOLD EXTRACTION

Gold has fascinated mankind since the memory of man. Initially, it was found as native gold in small nuggets where it had been deposited by rivers or streams. With the development of mankind and technology the methods of extraction changed. Gold was already recovered by concentration in 2500 BC . Before 500 BC gold was reclaimed by cupellation (separation of gold together with silver from lead and other metals) and before the Christian era it was already recovered by amalgamation. One of the earliest descriptions of gold being found in veins was in 2 BC. Crushing was initially performed by hand until the stamper was invented during the end of the 15th or beginning of the 16th century. Amalgamation was for a long time the principal method for gold extraction. During the California gold rush in 1848 stamping together with amalgamation was widely used.

In 1848 chlorine was used for the first time as an lixiviant in Silesia. But two years previously, a German chemist by the name of L. Elsner, discovered that gold was soluble in a dilute solution of potassium cyanide but did not realise the importance of his discovery. Later, a metallurgist by the name of J. S. McArthur discovered the practical use of the dissolution of gold in potassium cyanide and not much later the first plants using this method were in use. Amalgamation was a cheap method, but only about 60 % of the gold was extracted. With the ore grade decreasing, the mines changed over using pulp leaching, initially with aqueous chlorine which was later replaced by potassium cyanide. The leached pulp was filtered after which the gold was precipitated by cementation with zinc (Hertz).

1.2 THE CARBON-IN-PULP (CIP) PROCESS

The adsorptive properties of wood charcoal were known already by the Egyptians and the ancient Hindus for the purification of drinking water . In 1847 it was found that activated carbon adsorbed gold-chloride readily. By 1880, the process was patented by Davis in which, after the gold-bearing pulp was leached with chlorine, activated charcoal was used for the adsorption of the gold complex. In 1894, four years after McArthur found a practical use for Elsner's discovery of the dissolution of gold by aid of potassium cyanide, Johnson patented the process of using activated charcoal for the adsorption of gold from cyanided solutions. It has taken nearly eight decades before the validity of this process became recognised as a commercially valuable gold extraction process.

Through the amount of research and tests conducted on different types of activated carbon (peach pips, coconut shell, peat) which showed better adsorption properties, more abrasion resistance and better elution techniques, activated carbon became more accepted in the mining industry. The discovery of the Zadra elution process where hot caustic cyanide is used, the electrowinning on steel wool and the regeneration of the carbon were the most important discoveries that led to the breakthrough.

In 1961, the first fully integrated CIP plant was constructed at the Carlton Mill, Cripple Creek in Dakota, to recover the gold from the slimes fraction. The next one was in 1973 at the Homestake Mine in South Dakota. In South Africa CIP plants were built to treat all of the cyanided ore. A typical flow diagram is shown in Fig. 1.1 .

Elution of the gold-cyanide complex from the carbon surface can be performed in various ways. These include using inorganic and organic compounds. Zadra (1950) found that the adsorbed gold could be eluted efficiently using potassium cyanide and a hot (93° C) solution of sodium sulphide. This process was modified and the sodium sulphide was exchanged for sodium hydroxide (Zadra, Engelen and Heinen, 1952) so that gold and silver are eluted effectively. The gold and silver are then removed from the eluate using an electrowinning cell in series using steel wool as a cathode.

Anglo American Research Laboratories (AARL) method consists of a pre-treatment step of soaking the carbon in hot strong caustic and cyanide with the elution of the gold by de-ionised water (Davidson and Duncanson, 1977; Davidson and Veronese, 1979). Little or no elution of Ag, Cu, Ni and Zn was observed. Eluate is processed in an electrowinning circuit or zinc cementation is used.

Elution using organic solvents like ethanol, methanol, acetone and acetonitrile (Heinen, Peterson and Lindstrom, 1976; Martin *et al,* 1976; Flemming, 1983) found that gold stripped easily from activated carbon.

1.3 OBJECTIVES OF THE STUDY

As activated carbon is being used extensively as an adsorbent for the extraction of gold from cyanided pulp and the fact that cyanide can lead to certain environmental problems (especially with an worldwide increasing emphasis on the environment), the necessity was created for the investigation into alternative lixiviants for the leaching and adsorption of gold.

The environmental problems could be categorised as Manahan, 1991; Meyer, 1977):

- cyanide is a deadly poisonous substance.
- cyanide has a very high affinity for metal ions.
- cyanide ion forms a deadly hydrocyanic gas
- cyanide salts can posion both through inhalation as a gas or adsorbed through the skin

The halides are reagents that have been investigated in depth. Adsorption of gold from chloride and bromide solutions onto activated carbon has been performed at length by previous researchers (Hughes and Linge, 1989; Hiskey and Ramadorai, 1990; Hiskey and Qi, 1991; Pesic and Storhoc, 1992; Brown and Deschênes, 1993; Mensah-Biney *et al,* 1993; Sun and Yen, 1993) , but minimal work has been performed on the adsorption of gold from iodide solutions onto activated carbon. Therefore , the objective of this study, is to investigate the adsorption of gold from iodide solutions onto activated carbon, and highlight sensitive parameters that might influence such a system. It will also be important to propose a mechanistic model to predict the uptake of gold-iodide from solution.

The following aims were set for this project :

- To investigate possible factors influencing the adsorption process emphasising the effect of initial gold concentration, iodine/iodide concentration, pH , dissolved oxygen and stirring speed.
- To develop a simple kinetic model which can predict gold iodide adsorption onto activated carbon.
- To investigate the basic electrochemistry behind the formation of elemental gold on the carbon surface.

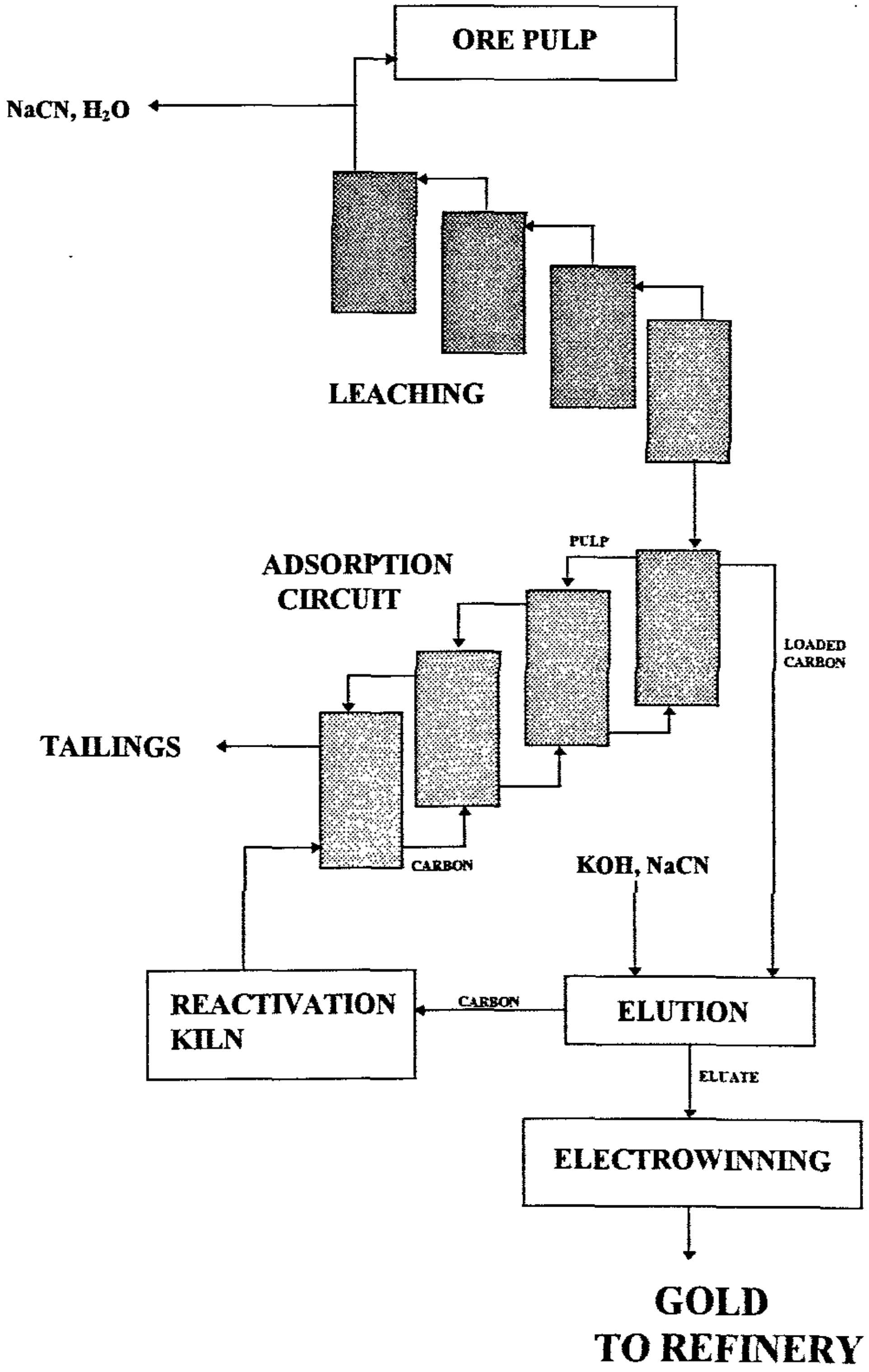


FIGURE 1.1 : Flow diagram of the Carbon In Pulp process

CHAPTER 2

LITERATURE REVIEW

2.1 DISSOLUTION OF GOLD

Hiskey and Atluri (1988) basically describes the dissolution of gold as an electrochemical model, with anodic and cathodic reactions. A mixed potential is developed between internally short circuited cathodic and anodic sites (Figure 2.1). With the dissolution of gold the anodic step involves the oxidation and complexation of the gold metal. It basically follows the following reaction :

$$Au + 2X \Rightarrow AuX_2^- + e^- \qquad (2.1)$$

where X is the complexing ligand.

The cathodic reaction entails the reduction of the oxidant (O):

$$O^{z+} + e^- \Rightarrow O^{(z-1)+} \qquad (2.2)$$

It is possible to oxidise Au(0) to Au(III) in the presence of a suitable complexing agent

$$Au + 4X \Rightarrow AuX_4^{3-} + 3e^- \qquad (2.3)$$

These are just general reactions. In order to have basic understanding in the chemistry of the aqueous gold solutions, the background of the gold leaching using different lixiviants (cyanide, chlorine, bromine and iodine) will be briefly investigated.

Under these halogens, the stability of the complexes increase as follows (Hiskey and Atluri, 1988). :

$$Cl^- < Br^- < I^-$$

Each lixiviant will be studied in the following paragraphs.

2.1.1 CYANIDE AS LIXIVIANT

Gold is readily dissolved in the presence of cyanide to form the stable linear cyanide complex, $Au(CN)_2^-$. There is no known formation of gold(I) cyano complex. The overall dissolution is given by the following reaction with dissolved oxygen as the oxidant (Hiskey and Atluri, 1988) :

$$4Au + 8CN^- + 2H_2O + O_2 \Rightarrow 4Au(CN)_2^- + 4OH^- \qquad (2.4)$$

As cyanide forms poisonous hydrocyanide gas in acidic media, the pH must stay above a level of 10. At this pH level, the potential of the complex is -0.52 V (SHE).

2.1.2 CHLORINE AS LIXIVIANT

Chloride leaching is a process that has already existed for many years,
The dissolution reactions of gold in chloride solutions are the following (Kelsall *et al*, 1992):

$$AuCl_2^- + é \Leftrightarrow Au + 2\ Cl^- \qquad (2.9)$$

$$AuCl_4^- + 3é \Leftrightarrow Au + 4\ Cl^- \qquad (2.10)$$

In solutions with a high concentration of Cl ions versus Au, the predominant complex would be dichloroaurate(I) (for example sea water 0.004 to 0.008 ppb. Au to 18.98 ppm. Cl^-), meanwhile ion predominates at standard electrode potential of 1.1 V and higher (Kelsal *et al*, 1993; Hiskey and Atluri, 1988). The tetrachloroaurate(III) can reduce by the following by the reaction :

$$AuCl_4^- + 3é \Leftrightarrow AuCl_2^- + 2\ Cl^- \qquad (2.11)$$

But the dichloroaurate(I) ions are unstable and disproportionate to the tetrachloroaurate(III) ion by the reaction which has a equilibrium constant of $10^{-7.68}$:

$$3AuCl_2^- \Leftrightarrow AuCl_4^- + 2Au + 2Cl^- \qquad (2.12)$$

The gold-chloro complex is stable up to a pH of 8. Dissolved chlorine, hypochlorous acid, hypochlorite ion and nitric acid are all capable to oxidise gold in a chloride media.

2.1.3 BROMINE AS LIXIVIANT

As with chlorine, Au(III) forms a more stable complex then the Au(I) in bromine solutions except for a narrow potential range. The reactions are as follows (Kelsall *et al*, 1992):

$$AuBr_2^- + é \Leftrightarrow Au + 2Br^- \qquad (2.13)$$

$$AuBr_4^- + 3é \Leftrightarrow Au + 4Br^- \qquad (2.14)$$

Both bromo complexes are more stable than the chloro complexes and up to a pH of 9 ($10^{-5.25}$). The disproportionation reaction of dibromoaurate(I) ions follows the following reaction (Kelsall *et al*, 1992) :

$$AuBr_2^- \Leftrightarrow 2Au + AuBr_4^- + 2\ Br^- \qquad (2.15)$$

Bromine can be considered as the oxidising medium for the dissolution of gold in acidic medium.

2.1.4 IODINE AS A LIXIVIANT

Iodine and iodide have been patented several times as a leaching material for extraction of gold from scrap material and in-situ leaching (Wilson 1973, Wilson 1974, McGrew and Murphy, 1985). The actual dissolution and leaching process of gold by iodine has been investigated in depth by various authors (Hiskey and Atluri , 1988 ; Hiskey and Qi, 1991 ; Davis and Tran, 1991 ; Qi and Hiskey, 1991 ; Kelsall *et al,* 1993 ; Davis, Tran and Young, 1993 ; Angelidis *et al,* 1993).

Hiskey and Atluri (1988) investigated the dissolution chemistry of gold and silver with different lixiviants . They stated that iodine demonstrate the existence of poly-halides. The tri-iodide is formed by the following chemical reaction

$$I_2(aq) + I^- = I_3^- \qquad (2.16)$$

The tri-iodide ion is present when the solution contains more then 1×10^{-3} M dissolved iodine. Therefore I_3^- can serve as an oxidant for gold according to the following electrochemical reaction

$$Au + 2I^- \Rightarrow AuI_2^- + é \qquad \text{anodic} \qquad (2.17)$$

or

$$Au + 4I^- \Rightarrow AuI_4^- + 3é \qquad \text{anodic} \qquad (2.18)$$

$$\underline{I_3^- + 2é \Leftrightarrow 3I^-} \qquad \text{cathodic} \qquad (2.19)$$

$$2Au + I_3^- + I^- \Rightarrow 2AuI_2^- \qquad \text{overall} \qquad (2.20)$$

or

$$2Au + 3I_3^- \Rightarrow 2\ AuI_4^- + I^- \qquad \text{overall} \qquad (2.21)$$

According to Kelsall *et al* (1993) iodine forms tetraiodoaurate(III) ions but with a wide area on the Pourbaix diagram where diiodoaurate(I) is stable. These complexes are both stable up to pH 14 as shown in Figure 2.2. Other oxidants like oxygen and hydrogen peroxide have almost no effect on the reaction rate nor NaCl concentration or pH in the range 2-10.

According to Davis and Tran (1991), dissolution of gold in iodide-iodine solutions is dependent on the solution pH and concentrations of iodine and iodide. The gold oxidation half reaction has a higher rate at an increasing iodide concentration and is affected by the pH of the solution. The dissolution of gold decreases progressively from a pH above 10. This agrees with Figure 2.2 where at pH 10 there is only a stable zone for AuI_2^-. From pH 11 upwards the predominant oxidising species namely tri-iodide is not present anymore (Figure 2.3) and therefore no oxidation occurs.

Qi and Hiskey (1991) investigated the kinetics of the gold dissolution in iodide solutions and came to the same conclusions as above and also compared the rate of dissolution of gold in iodide solutions with cyanide solutions. Solutions containing 1×10^{-2} M NaI and 5×10^{-3} M I_2 have nearly the same dissolution rate as a solution containing $> 2.7\times10^{-3}$ M KCN with air as an oxidant.

2.1.4.1 PROCESS CONSIDERATIONS

Mc Grew and Murphy (1985) patented the process for iodine leach for the dissolution of gold. To a solution concentrated with natural salts, elemental iodine is added until saturated, whereupon the mineral sulphides in the ore zone charged with this solution react with the iodine to form iodide. This lixiviant is circulated through the ore zone until all the gold is dissolved. The gold is subsequently adsorbed onto activated charcoal. The excess iodide formed is recycled to iodine electrochemically in a special diaphragm cell to regenerate the lixiviant.

The ore zone reactions are the following :

$$FeS_2 + 7I_2 + 8H_2O \Rightarrow Fe_2^+ + 2SO_4^{2-} + 16H^+ + 14H^+ + 14I^- \qquad (2.22)$$

$$FeS_2 + I_2 + H_2O \Rightarrow Fe_2^+ + 2S + 2I^- \qquad (2.23)$$

Hiskey and Qi (1991) investigated the leaching behaviour of gold in iodide solutions where they also looked at process considerations. They stated that gold extraction from oxidised and semi-refractory ores can be accomplished using dilute iodine/iodide solutions. At pH 5 and 3×10^{-2} M NaI and 5×10^{-3} M I_2 at 25° C gold will dissolve approximately 3.5 times faster than by cyanidation. But they stated that the success for this process will depend on the effective gold recovery from the iodide solution. As iodine is an expensive reagent, it would be applicable to use low concentration solutions and that the reagent can be regenerated cost effectively for recycling.

2.2 ACTIVATED CARBON

2.2.1 Physical properties

Activated carbon is a universal name for a wide range of carbonaceous substances (usually of biological origin, e.g. wood, peat, coconut shell, fruit stones, coal, charcoal) which has a high carbon content. It usually has a large internal surface due to a porous structure. The production process consists out of two principal processes, namely carbonisation and activation.

The carbonisation process involves the heating of the source material to 400-700° C in an inert atmosphere. Here the carbonaceous material undergoes pyrolysis whereby most hetero atoms (O, N, S, etc...) are volatilised. The carbon atoms usually form polycyclic aromatic structures that are grouped together in randomly oriented and crosslinked sheets.

The activation process involves the further heating of the substance to 800-1100° C in the presence of an oxidising gas like steam, air or carbon dioxide. These gases mostly react with the most reactive parts of the carbon structure which are at the edges of the microcrystallites and at defects in the crystal lattice. This leads to the formation of functional groups on the carbon surface and inside the pores. An activated carbon particle contains a complex network of pores (Figure 2.4). These can be grouped according to their diameters. McDougal and Hancock (1980) defines the pore size distribution as:

1. Micropores r = 0.8 - 5 nm
2. Mesopores r = 5 - 50 nm
3. Macropores r = 50 - 2000 nm

The macropores serve essentially as transport "ducts" by diffusion to the meso- and micropores where most of the adsorption occurs

2.2.2 ELECTROCHEMICAL PROPERTIES

The electrochemical properties of activated carbon are difficult to quantify, as the chemical surface properties of activated carbon are dependent on the material origin of the carbon and the activation method. Several publications focus on the electrochemical properties of the activated carbon surface. Jankowska *et al* (1981) postulated that the ions bonded to the activated carbon surface by electrochemical adsorption. Garten and Weis (1957) reported that electrolyte adsorbed onto activated carbon by chromen groups on the carbon surface. Cyclic voltametry on activated carbon led to the conclusion that quinone-hydroquinone couple is responsible for the potential response (Puri; 1970). Jankowska *et al* (1981) brought forward that activated carbon in a electrolyte solution containing halides of a specific anion adsorption occurred with a partial exchange of charge between the adsorbed ion and the carbon surface. This exchange was the greatest for iodide ions. Therefore, the potential of the carbon was strongly dependent on the kind of anion present in the solution and decreases with the increasing concentration of the solution. It was further stated that the adsorption of the ions probably displaced an adequate amount of hydroxyl ions from the double layer resulting in the alkalisation of the electrolyte solution. Furthermore, Frumkin *et al*, (1940) stated that the growth of the potential of carbon immersed in an electrolyte solution is due to the electro-reduction of the adsorbed oxygen.

Electrochemical studies on activated carbon electrodes (Marsh, 1994) identified that the electro-active groups on the surface of the activated carbon electrode are of the quinone-hydroquinone type. Furthermore, the comparison between a polished and air activated glassy carbon electrode and an "average" activated carbon, showed that the glassy carbon could be used as model substrate for an activated carbon surface based on :

1. structural similarities with activated carbon,
2. the presence of carbon-oxygen surface functional groups and
3. the creation of large relative surface areas

2.3 ADSORPTION ONTO ACTIVATED CARBON

2.3.1 GOLD FROM CYANIDE SOLUTIONS

The adsorption of gold from cyanide solutions onto activated carbon has been investigated and published extensively by numerous researchers/authors. There are different mechanisms proposed, namely :

- reduction of $Au(CN)_2^-$ to gold metal
- adsorption of the $M^{n+}[Au(CN)_2]_n$ ion-pairs
- AuCN precipitation from degradation of $Au(CN)_2^-$
- double-layer adsorption of $Au(CN)_2^-$ and cations onto charged surfaces, with the partial reduction of the gold complex to cluster type series

Adams (1990) came to the conclusion that several different adsorption mechanisms are possible. Firstly, under high ionic strength and pH levels of more then 7, the aurocyanide is adsorbed on activated carbon via an ion-pair mechanism, where $M^{n+}[Au(CN)_2]_n$ is adsorbed onto the carbon surface without any change. Meanwhile, under conditions of low ionic strength and pH levels above 7, the concentration of oxygen controls the type of mechanism, namely :

1. adsorption of the ion-pair mechanism in absence of oxygen
2. ion-exchange adsorption of the gold cyanide in the presence of oxygen

2.3.2 GOLD FROM BROMINE SOLUTIONS

Mensah-Biney *et al* (1993) stated that gold is adsorbed from a gold bromide solution by mass transfer of $AuBr_4^-$ from the solution to the carbon surface and the reduction of the adsorbed gold complex to metallic gold. The predominant mechanism during the initial period is mass transfer from solution to the carbon surface and the reduction is the predominant mechanism during the slow period of loading. The reduction can be described as follows :

$$4\ AuBr_4^- + 3C + 6H_2O \Rightarrow 4\ Au + 3CO_2 + 12\ H^+ + 16\ Br^- \qquad (2.24)$$

Meanwhile, Pesic and Storhoc (1992) came to the conclusion that gold bromide adsorbs in its original ionic form, $AuBr_4^-$. This is most probably due to the fact that they used an initial gold concentration of 5 $mg.l^{-1}$, while Mensah-Biney *et al* (1993) worked in a concentration region of 25 - 100 mgl^{-1} . This means that in the experiments of Pesic and Storhoc (1992) the carbon in contact with the gold solution had an abundance of active sites available for ion-exchange.

Further, they indicate that pH levels lower then 6 have no influence on the adsorption, while higher pH levels had a negative influence. Bromine concentration influences the gold adsorption negatively as it competes with the gold on the carbon.

2.3.3 GOLD FROM CHLORINE SOLUTIONS

The adsorption of gold has been investigated by several authors (de Siegel and Soto, 1984; Huges and Linde, 1989; Hiskey and Jiang, 1990; Sun and Yen, 1993, Brown and Deschênes, 1993). All of these authors conclude that the gold chloride complex is reduced on the activated carbon surface by the following reactions:

$4AuCl_4^- + 3C + 6H_2O \Leftrightarrow 4Au + 3CO_2 + 12H^+ + 16Cl^-$ $E_o = 0.796$ V (2.25)

$4AuCl_2^- + C + 2H_2O \Leftrightarrow 4Au + CO_2 + 4H^+ + 8Cl^-$ $E_o = 0.948$ V (2.26)

De Siegel *et al* (1994) analysed microscopic observations on adsorption of metallic gold onto activated carbon using gold dissolved in an acid chloride media. Their observations concluded that gold is adsorbed on the activated carbon surface in spherical particles ranging in diameter from ~ 0.5 to 35 μm and which is dependent on the gold concentration in solution. Gold channelling through the carbon particle could not be detected and they stated that with fine radials filled with gold in conjunction with the superficial gold ring that surrounds the carbon particles in section, that equilibrium had been achieved between the carbon particle, the adsorbed gold and the liquid phase. It was also said that experimental evidence showed that an acidic media is more favourable for adsorption than basic media.

Hughes and Linge (1989) demonstrated that the adsorption of the gold chloride complex is governed by first-order kinetics and that the reaction is controlled by either mass transfer or a first-order surface reaction. With the rate constant being dependent on the solution stirring rate, it is led to believe that the mass transport step is controlling or sharing the control of the reaction.

Equation 2.25 can be expressed as complementary cathodic and anodic steps as illustrated in the next reactions :

$$AuCl_4^- + 3e^- \Rightarrow Au + 4Cl^- \qquad (2.27)$$

$$C + 2H_2O \Rightarrow 4H^+ + CO_2 + 4e^- \qquad (2.28)$$

The standard potential (theoretical) for reaction (2.28) is 0.21 V. So, on the basis of thermodynamics, it could be predicted that activated carbon would reduce gold to the metallic state in a gold-chloride system. This would be analogous to an electrochemical cementation reaction. A schematic representation is shown in Figure 2.5.

They further concluded that gold chloride is reduced to the metallic state at the carbon surface and is not molecularly adsorbed by the carbon. Gold was found to reduce in patches on the carbon surfaces, especially at edges and other surface irregularities. Adsorption experiments conducted with different initial gold concentration showed that the rate of gold reduction appeared nearly independent of the initial concentration. This was concluded by using the following general first order rate expression for gold reduction :

$$\frac{d\left[Au(Cl)_4^-\right]}{dt} = -\frac{k_f A\left[Au(Cl)_4^-\right]}{V} \qquad (2.29)$$

Where $[Au(Cl)_4^-]$ is the gold chloride concentration (ppm), t is time (s), k_f is the rate constant (mass transfer coefficient) (cm.s^{-1}) which is equal to $\frac{d}{dx}$ for boundary layer diffusion, A is the area (cm^2) and V is the solution volume (cm^3).

Tests conducted in the presence of sodiumhypochlorite (NaClO) indicated that the reduction rate becomes more sensitive due to the destruction of the active sites on the carbon by the hypochlorite. Gold adsorption tended to be independent at pH levels under 7, while at a higher pH level there is a gradual decrease in the level of gold extraction. with the addition of iodide to the gold chloride solution, the following equilibrium takes place in the solution :

$$AuCl_4^- + 4I^- = AuI_4^- + 4Cl^- \qquad (2.30)$$

Carbon can reduce the auric iodide complex. With the addition of iodine it appeared that with an increasing iodide concentration the extraction of gold from the solution tended to shift to an adsorption type of reaction.

Sun and Yen (1993) concluded that the reduction of gold from acidic chloride solutions behaved as a first-order reaction. Furthermore, an increase in the concentration of aqueous chlorine decreased the gold adsorption due to the re-dissolution of the gold from the carbon surface by the aqueous chlorine. Brown and

Deschênes (1993) used X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD) and Electron Probe Micro-Analysis (EPMA) to characterise chemically the gold complex adsorbed on activated carbon from gold chloride solution and other systems. They concluded that gold is reduced to metallic state when adsorbed on carbon from acidic chlorinated solution as has been discussed, but that a portion of the gold adsorbed remained in cationic form as a $AuCl_4^-$ complex.

Electrochemical studies of the nature of gold adsorbed from tetrachloroaurate on glassy carbon surfaces (Marsh, 1994) led to the speculation that the gold complex adsorbed via two mechanisms. Firstly, in solutions of low ionic strength (i.e. in the absence of supporting electrolyte) and in the presence of oxygen the adsorption tends to occur as a combination of ion exchange and the reduction of the complex onto the carbon surface. Meanwhile, in solutions of high ionic strength, the gold chloride tends to be reduced on the carbon surface.

2.3.4 GOLD ADSORPTION FROM IODINE SOLUTIONS

The adsorption of gold from iodine solutions has not been investigated in depth. Hiskey and Qi (1993) investigated the nature of gold uptake from iodide solutions by carbon. They found that carbon is extremely effective in extracting gold from iodide solutions. The adsorption follows Freundlich-type isotherms. Maximum loading behaviour is similar to that for gold cyanide. They further found that the loading is sensitive to the presence of iodine and the availability of active sites. Scanning Electron

Microscopy showed that metallic gold is deposited on the carbon surface, while Tunnelling Electron Microscopy indicated that extremely small particles of gold disseminated inside the carbon matrix. According to them, this might indicate the combined reduction- and adsorption process, whereby some gold is deposited on the carbon surface and some adsorbed in the porous structure.

2.3.5 IODINE ADSORPTION

Baba *et al* (1985) investigated the characteristics and mechanisms for the adsorption of iodine from aqueous solutions and organic solvents onto activated carbon. Their results indicate that the amount of iodine adsorbed decreases with the increase in potassium iodide concentration which is attributed to the increase in solubility of iodine. Furthermore, it has been concluded that iodide ions is hardly adsorbed on activated carbon from iodine-potassium iodide solutions. Meanwhile, Jankowska *et al* (1981) stated that iodine adsorbs strongly on the activated carbon surface by the mechanism of ion exchange.

2.4 SIGNIFICANCE OF THE LITERATURE REVIEW

The literature review shows clearly that there is a lack in the research on the adsorption of gold complexes onto activated carbon, especially from halide solutions.

Meanwhile, as cyanide is the major lixiviant used in the gold mining industry, the adsorption of gold cyanide on activated carbon has been investigated thoroughly. Several researchers have investigated the dissolution of gold in halide solutions and the adsorption of gold-chloride and bromide, but relatively minimal work has been undertaken in investigating the adsorption of gold from iodine/iodide solutions. Except for one paper, no work has been published on the adsorption of gold from iodine/iodide solutions.

An attempt will be made to explain the adsorption mechanism and the nature of the gold adsorbed onto activated carbon from iodine solutions.

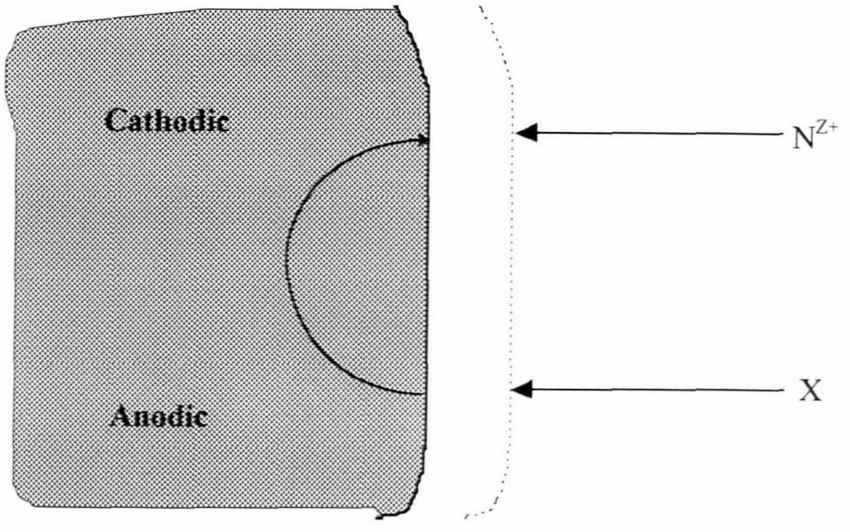


FIGURE 2.1 Schematic of the electrochemical microcell describing the dissolution of gold. (Brent and Atluri, 1988)

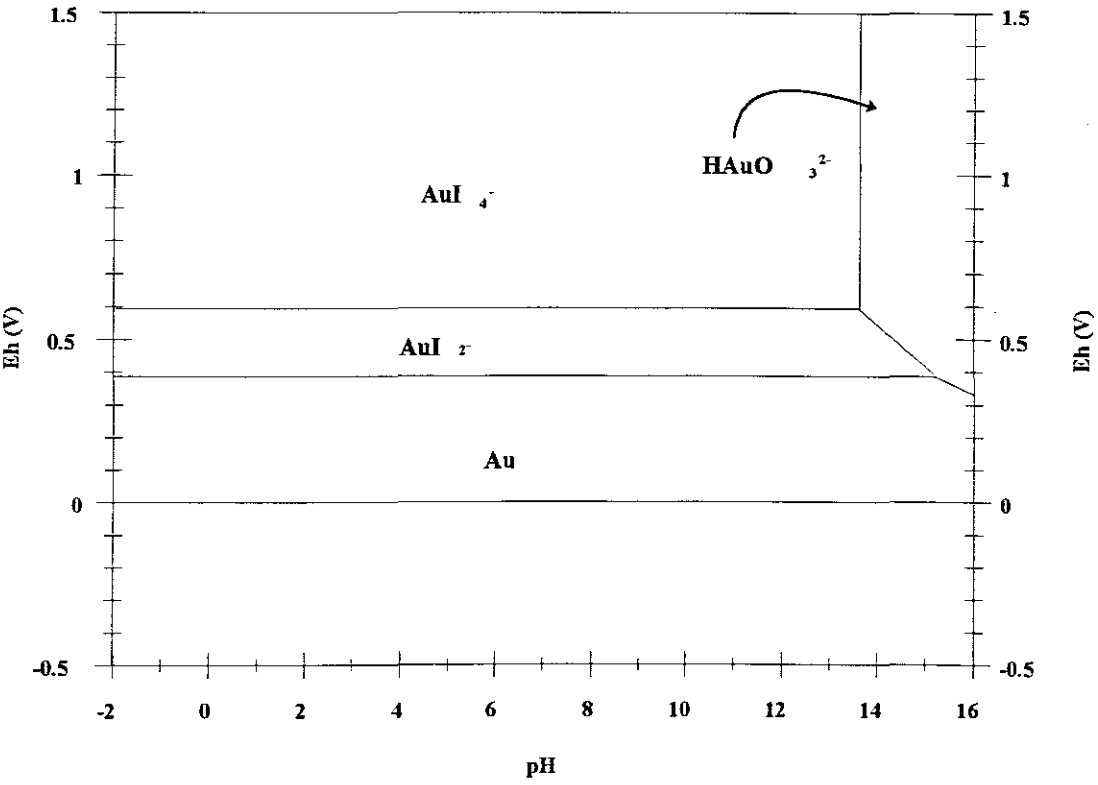


FIGURE 2.2 : Eh-pH equilibrium diagram for gold-iodide/water system [Au] = 10^{-5} and [I$^-$] = 1 M

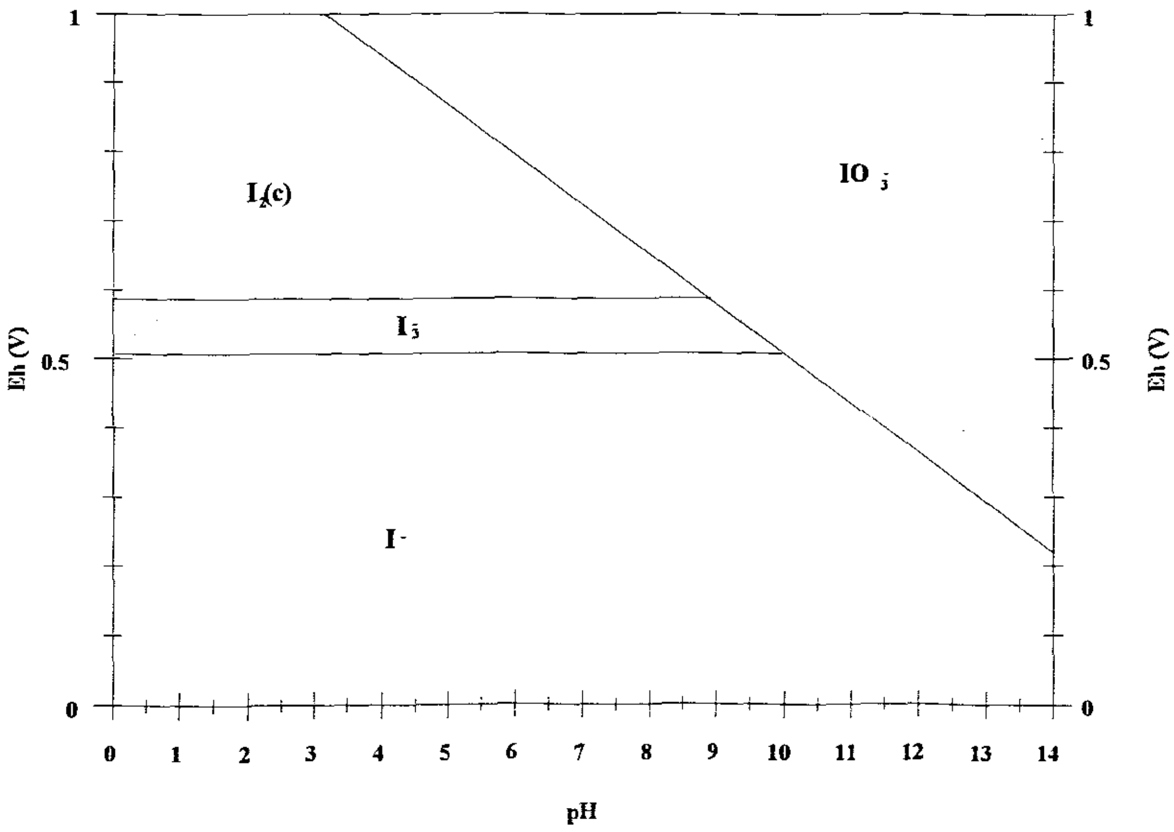


FIGURE 2.3 : Eh-pH equilibrium diagram for iodide/water system [I$^-$] = 1 M

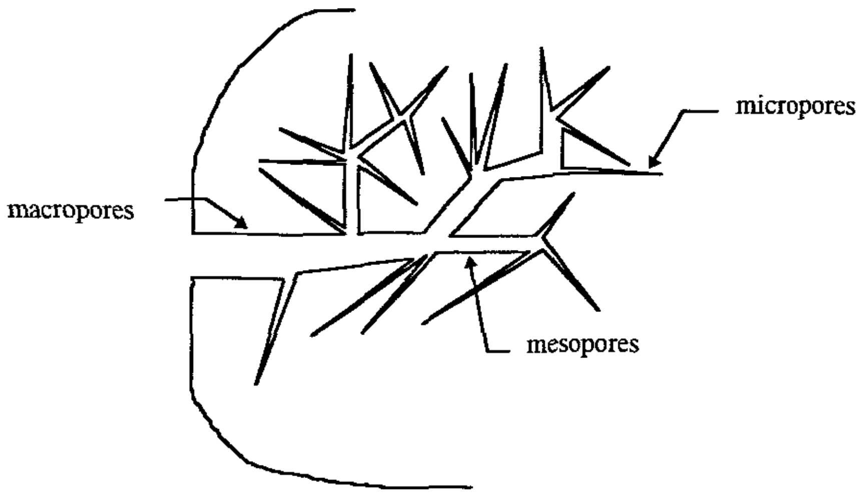


FIGURE 2.4 : Schematic representation of the porous structure of an activated carbon particle

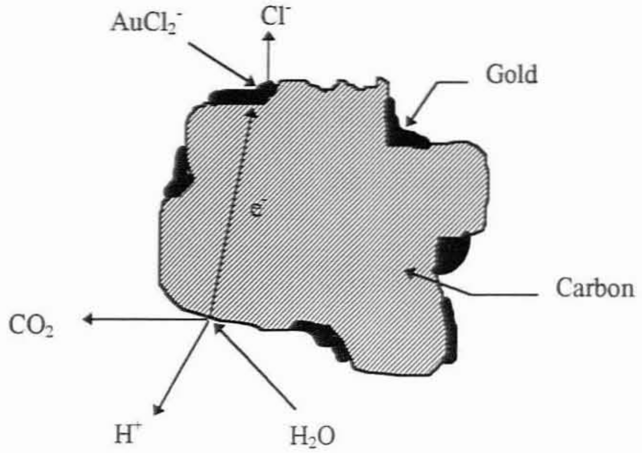


Figure 2.5 : Schematic representation of the electrochemical reduction of gold at a carbon surface (Hiskey and Jiang, 1990)

CHAPTER 3

ADSORPTION KINETICS

In this chapter the film diffusion mechanism will be discussed, which will be similar to the model used by Johns (1987) for the adsorption of gold cyanide onto activated carbon.

3.1 ASSUMPTIONS

These established film diffusion rate are derived on the following assumptions :

- interdiffusion in the film is treated as quasi-stationary (film diffusion is relative fast compared to the concentration changes at the carbon boundary)
- the film is treated as a planar layer (one dimension diffusion)
- the carbon particles can be treated as equivalent spheres with a homogeneous surface

3.2 EQUILIBRIUM

The equilibrium isotherm indicated that the adsorption of gold-iodide followed the Freundlich isotherm. The one step reaction mechanism verified that film diffusion was the predominant adsorption mechanism. This will be discussed in Chapter 5. Taking these factors into consideration, we can derive the following equations to model the film diffusion.

Freundlich equilibrium follows the ensuing equation :

$$Q_s = AC_s^n \tag{3.1}$$

Which can be rewritten as follows :

$$C_s = \left[\frac{Q_s}{A}\right]^{\frac{1}{n}} \tag{3.2}$$

Fick's law states that the flux through the film ($\tilde{n}_L$) is equal to the change in concentrations from solution to the carbon surface multiplied with the film diffusion coefficient.

$$\tilde{n}_L = k_f(C-C_s) \tag{3.3}$$

or the total mass balance over the reactor

$$-V\frac{dC}{dt}=\tilde{n}_L A \qquad 3.4$$

The surface area A of the particle can described as follows :

$$A=\frac{6M}{\rho d_p} \qquad 3.5$$

the combination of equations 5.3, 5.4 and 5.5 yield :

$$-V\frac{dC}{dt}=\tilde{n}_L\frac{6M}{\rho d_p} \qquad 3.6$$

$$-V\frac{dC}{dt}=k_f\left(C-C_s\right)\frac{6M}{\rho d_p} \qquad 3.7$$

$$\frac{dC}{dt}=\frac{6Mk_f}{\rho d_p V}\left(C_s-C\right) \qquad 3.8$$

$$\frac{dC}{dt}=\frac{6Mk_f}{\rho d_p V}\left(\left[\frac{Q_s}{A}\right]^{\frac{1}{n}}-C\right) \qquad 3.9$$

$$\frac{dC}{dt}=\frac{6Mk_f}{\rho d_p V}\cdot\frac{Q_s^{\frac{1}{n}}}{A^{\frac{1}{n}}}-\frac{6Mk_f}{\rho d_p V}\cdot C \qquad 3.10$$

let $A^{1/n}=B$, and the loading of the carbon surface Q_s is equal to

$$Q_s = \frac{(C_i - C)V}{M_c} \qquad 3.11$$

then

$$\therefore \frac{dC}{dt} = \frac{6Mk_f}{B\rho d_p V}\left[\frac{\left(C_i - C_{(t)}\right)V}{M_c}\right]^{\frac{1}{n}} - \frac{6Mk_f C_{(t)}}{\rho d_p V} \qquad 3.12$$

Where $\frac{dC}{dt}$ is the change in concentration of gold-iodide in solution over time.

3.3 NUMERICAL SOLUTION

A computer program using fourth order Runge Kutta (Appendix A) routine was used to solve equation 3.12 . Model predictions are presented graphically in Chapter 5.

CHAPTER 4

EXPERIMENTAL

4.1 Experimental Materials

Due to the high cost of gold(I)-iodide crystals, the gold iodide solution was made up by dissolving pure gold nuggets in an iodine/iodide solution. This was accomplished by dissolving 1 g pure gold (99.99% Au) in a 1 L volumetric flask. The iodine/iodide solution was made up by combining 0.1 mole potassium iodide and $5x10^{-3}$ mole of pure iodine crystals which were dissolved in a 1 L volumetric flask. After the flattened gold nuggets were added, the solution was stirred on a magnetic stirrer for 3 days, or until no solid gold could be visually noticed anymore. The chemistry is explained in the previous chapter. This solution had a final Au concentration of 1000 ppm or $1g.L^{-1}$. This gold-iodide solution was kept in a cupboard to minimise the effect of light on the solution.

All chemicals used were of analytical grade (Merck) and the water used throughout all experiments was double distilled and had a pH level of 6.5.

The pH level during the experiments was controlled by the addition of a 1 M KOH or a 1 M HCl solution.

One type of coconut shell based activated carbon was used, provided by ACIX. Only a size fraction of 1.4 mm was used. The activated carbon had a density of 800 $kg.m^{-3}$ and a surface area of 1020 $m^2.g^{-1}$.

Before the experiments, the carbon was washed in a mild acidic (HCl) solution and then thoroughly rinsed with distilled water. The carbon was oven dried and kept in a closed flask.

4.2 Batch experiments

All the adsorption experiments were performed in a baffled reactor vessel. This batch reactor (Figure 4.1) was made out of perspex with a height of 150 mm and a diameter of 100 mm and three evenly spaced baffles of 10 mm width. The solution was agitated by a perforated flat blade impeller made out of stainless steel which was driven by a Heidolph variable speed overhead stirrer.

For each test, the dry weighed carbon was soaked in water before brought in contact with the gold-iodide solution, as to minimise the effect of the escaping air from the porous structure on the film around the carbon particle, and to make sure that all the carbon particles were submerged in the solution. The carbon was then brought in contact with the gold-iodide solution. The stirring rate was kept at 300 rpm as this is the minimum speed necessary to keep all the activated carbon particles suspended. Samples (± 3 ml) of the solution were taken at specific time intervals and stored in glass vials for further analysis.

For the investigation of the effect of iodine on the surface of the activated carbon, experiments were conducted where the activated carbon was pre-treated in a concentrated iodine/iodide solution for 72 hours. Some of this carbon was further treated with sodium thiosulphate as to ensure no iodine is left on the surface and inside the pores of the activated carbon.

The effect of dissolved oxygen on the adsorption of the gold-iodide was examined by saturating the solution with oxygen (to raise the dissolved oxygen level) or with nitrogen (to lower the dissolved oxygen level). This was obtained by drilling a hole through the bottom (Figure 4.2) and connecting it with an oxygen or nitrogen bottle and bubbling the gas through the liquid at an approximate rate of ±10 ml per minute.

Equilibrium experiments were conducted by using different weights of carbon in contact with a Au solution (range of Au concentration : 5-50 ppm). The duration of the experiments was three weeks and samples were taken periodically as to monitor the approach of the equilibrium concentration.

4.3 ANALYTICAL METHODS

For the analysis of the Au concentration of the solution, a Varian Techtron AA-1275 was used with an air-acetylene flame with readings taken at an absorbance peak of 242.8 nm.

The dissolved oxygen levels of the solutions were measured using a Hanna HI 8043 dissolved oxygen meter. The pH levels of all the solutions were measured with a Beckmann Φ 71 using a combination Beckmann electrode. The potential of the solution was measured by the potential difference between a saturated (KCl) calomel electrode and a platinum or glassy carbon electrode with the aid of a Test 2010 multimeter. All experiments were performed at room temperature (± 25° C)

The scanning electron photographs were taken with HITACHI S- 405 A scanning electron microscope attached to a EDAX system for the identification of the elements present on the carbon surface. The results of these experiments will be discussed in chapter 5.

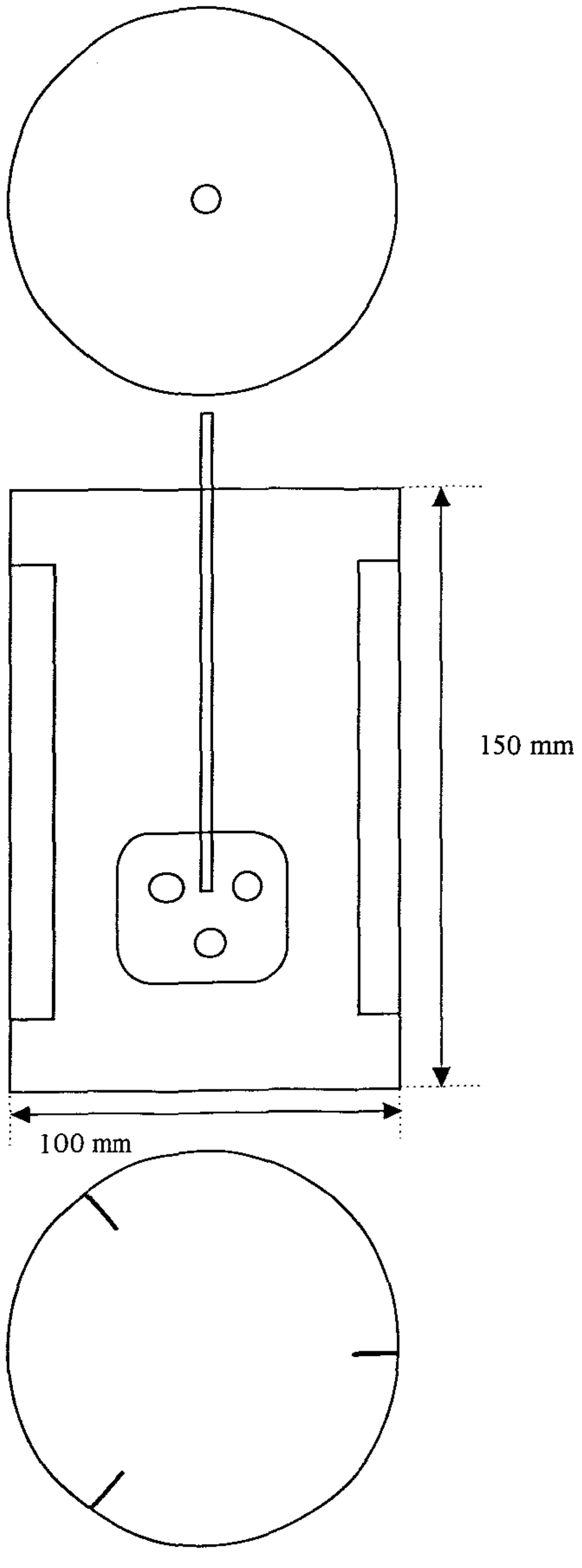


FIGURE 4.1 : Diagram of the batch reactor and impeller

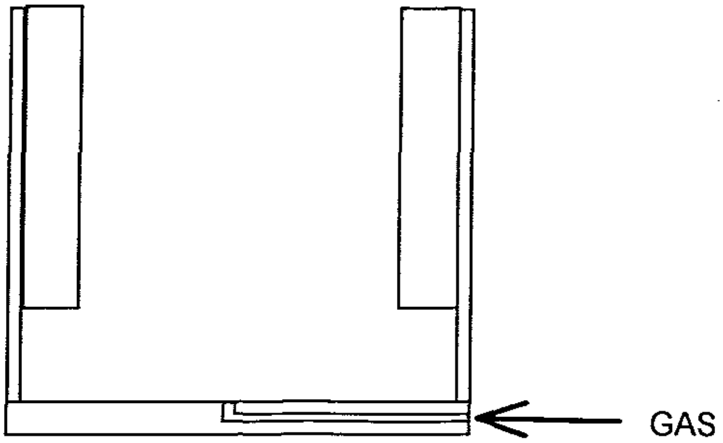


FIGURE 4.2 : Gas inlet for batch reactor

CHAPTER 5

FACTORS INFLUENCING THE ADSORPTION

In this chapter the effect of different conditions on the kinetic and equilibrium parameters of the adsorption of gold-iodide onto activated carbon were investigated. In each Figure containing adsorption curves, a reference “standard” adsorption curve is included as to highlight the change in the parameters. This curve is obtained by contacting the standard solution, with an initial Au concentration of 20 ppm to 0.2 g of activated carbon.

5.1 Mixing

In order to define the driving mechanism behind the adsorption of the gold-iodide complex adsorption experiments were conducted at different impeller stirring speeds. From a preliminary test it was seen that the gold concentration dropped relatively fast versus the same experiment using gold cyanide. This was a first indication that film diffusion might play a pivotal role in the adsorption mechanism. The dependence of the rate constant on the stirring speed is a strong indicator that the mass transfer step is a controlling or sharing step in the control of the adsorption reaction.

The stirring rate influences the rate of mass transfer of gold-iodide from the solution to the carbon surface. The reason behind this is that the increase in stirring speed decreases the film layer thickness surrounding the carbon particle (Van Deventer ,1985). This decrease in thickness will decrease the film diffusion coefficient (k_f) in a film diffusion model.

The adsorption tests were performed at five different stirring speeds with samples taken at regular intervals for the first 30 min. with an initial gold concentration of 20 ppm for all the experiments.

As explained by Van Deventer (1985), to determine the film diffusion coefficient K_f, a plot of $\ln(C_s^o/C_s)$ versus time yields a straight line that passes through the origin. The k_f value can be determined from the slope of this line (Equation 5.1).

$$\ln\left(\frac{C_s^o}{C_s}\right) = \frac{6k_f m_c}{\rho d_p V_s}t, \qquad \text{as } t \rightarrow 0 \qquad (5.1)$$

Figure 5.1 shows the plot of the logarithm of C_o/C versus time, yielding a straight line, confirming the first-order kinetics. The gradient of the slope of each line was obtained by using Equation 5.1 which yielded the film diffusion coefficient. Figure 5.2 shows a plot of these coefficients (Table 5.1) obtained, against the impeller speed. This line for the gold-iodide yields a straight line indicating that film diffusion remains the primary mechanism of mass transfer. If at any time intra-particle diffusion would become dominant, this line would plateau of where the intra-particle diffusion would take over.

To ascertain that film diffusion is the dominant mechanism, an interruption test is a useful method to differentiate between intra-particle diffusion and film diffusion. After 1½ hours in a normal adsorption test, the carbon was removed from the solution, and replaced back into the solution after 1½ hours (Figure 5.3). If any intra-particle diffusion had taken place, this separation time would allow mass transfer to continue and phase over into intra-particle diffusion. Thus the gold-iodide would diffuse further into the pores, thus creating a higher driving force for mass transfer immediately after the re-immersion of the carbon in the solution. As seen from Figure 5.3 it is clear that no increase in kinetics takes place after the re-addition of the carbon to the solution. This confirms that film diffusion is the prominent mechanism in operation.

5.2 Initial gold concentration

Adsorption tests were conducted by contacting the same mass of activated carbon under similar conditions to solutions with different initial gold concentrations (Figure 5.4). The results indicated strongly that gold reduction takes place. In a gold cyanide solution, a higher initial gold concentration, would give a higher concentration gradient over the film thereby the highest initial gold concentration would give the highest adsorption rate. In the case of gold-iodide the adverse takes place. The higher initial gold concentration has a lower adsorption rate and equilibrium point. This is a strong indication that reduction of the gold complex takes place on the carbon surface. Fitting of the film diffusion model shows that during the initial stages of adsorption, the rate of film diffusion (Table 5.2) is the same for all concentrations, as indicated by Hughe and Linge (1989) and Hiskey *et al* (1990) for chloride solutions. The slower equilibrium loading can be attributed to two reasons : firstly, the depletion of active sites on the carbon surface as nearly no gold complex diffuses internally into the carbon, and secondly, the "shielding" by the reduced gold on the carbon surface. At higher initial gold concentrations, it seems like that the adsorption mechanism tends to become intra-particular, which can explain why Hiskey *et al* (1993) found some gold deposits inside the carbon matrix.

5.3 Iodine/iodide concentration

The solubility of iodine in aqueous solutions is strongly dependent on the iodide concentration. On the dissolution of iodide (Equation 5.2), poly-halides are formed of which the tri-iodide is the dominant species. This ion is the principal oxidising species in the aqueous iodine/iodide system.

$$I_2\,(aq) + I^-\,(aq) \Leftrightarrow I_3^- \qquad (5.2)$$

Figure 5.5 shows the adsorption profiles with different iodine, iodide, tri-iodide concentrations. In the standard solution, there were no free iodine crystals present. In the order to oxidise all the iodine present, sodiumthiosulfate was added to the solution to obtain a solution with only the gold complex and iodide present. For higher concentrations of iodine, 0.01 mole and 0.02 mole of iodine crystals was added to the solution. As seen in Figure 5.5, it can be clearly deduced that the iodide/iodine concentrations affect the kinetic and equilibrium parameters notably (Table 5.3) and the following explanations are offered :

1. For the case of an increase in iodine concentration
    a) As the iodine concentration increases, the tri-iodide concentration would also increase. This will lead to competitive adsorption between the aqueous iodine, tri-iodide and the gold-iodide.
    b) With the increase in iodine concentration, the tri-iodide concentration would also rise and, as it is the principal reducing agent, it would simply re-dissolve the gold reduced from the carbon surface.
    c) Also, with tri-iodide been a strong oxidising agent, Figure 5.6 shows clearly the degradation of the activated carbon surface which is most probably caused by the tri-iodide. This will obviously influence the active sites and reduction sites on the carbon surface.

2. For the case of decrease in the iodine concentration
    a) As no iodine and neither tri-iodide is present in the solution, the adsorption kinetics and equilibrium are much faster and lower respectively. This is against the expectations as Jankowska *et al* (1981) indicated that iodide ions get easily adsorbed onto activated carbon and actually change the electrochemical potential of the carbon in solution.

The adsorption curve shows clearly that iodide ions hardly influences the adsorption of gold-iodide. This may be due to the fact that the iodide adsorption is negligible compared to gold -iodide adsorption.

5.4 Pre-treated carbon

In order to observe if the iodine, iodide and tri-iodide play any significant role on the activated carbon surface, batches of activated carbon was pre-treated in a iodine/iodide solution for a time period of 72 hr. One batch was then further treated with sodiumthiosulphate, so as to oxidise all the iodine present on the activated carbon to iodide. This batch of carbons were then contacted with gold-iodide.

The results obtained indicate that the main competitive adsorption is between iodine, tri-iodide and the gold complex, as Figure 5.7 shows clearly that where the carbon was further treated with sodiumthiosulphate, the kinetics and equilibrium of adsorption coincide more or less with the "standard" adsorption curve (non-pre-treated carbon). This implies further, that the oxidising properties of the tri-iodide onto the carbon surface itself does not play a role in the adsorption/reduction of the gold-iodide complex. The only other significant role that the tri-iodide ion might play is on the re-dissolution of the reduced gold metal from the carbon surface.

5.5 pH levels

The pH level of the solution has an effect on the adsorption kinetics of metal halide complexes onto activated carbon (Sun and Yen, 1993; Pesic and Storhoc, 1992; Brown and Deschênes, 1993; Hiskey *et al*, 1990).

During these experiments, carbon was contacted with gold iodide solutions at three different pH levels, namely pH 2, 6.5 and 11. The adsorption curves (Figure 5.8) indicates the two different methods of adsorption, namely the ion exchange between the carbon and the gold-iodide ion and the reduction of the gold complex onto the carbon surface. The electrochemistry behind this will be explained in the next chapter (Chapter 6). Figures 5.9 and 5.10 show clearly the increase in gold reduction with an increase in pH. At pH 11, we have fast kinetics and low equilibrium point (Table 5.4). This is due to the fast reduction of the gold complex onto the carbon surface, thereby creating a strong driving force for film diffusion. Meanwhile, at pH 6.5 and 2, the acidic media favours the ion exchange of the OH^- from the hydroquinone type of active groups on the carbon surface with AuI_4^- in solution.

5.6 Dissolved oxygen concentration

During these experiments, the solution was pre-treated with oxygen and nitrogen. An hour before the carbon was brought into contact with the solution, oxygen or nitrogen was bubbled through the solution at a constant rate of 10 cm^3s^{-1} . For the case where oxygen was bubbled through the solution, the concentration of dissolved oxygen settled at 32 ppm, whereas, when nitrogen was bubbled through, the concentration fell to 0.1 ppm. The standard solution has a dissolved oxygen level of 7.8 ppm..

The concentration of dissolved oxygen had a relative small effect on the adsorption kinetics and equilibrium point (Figure 5.11). However, from the perspective of the reduction of the gold complex, it plays a significant role. Conferring the electron micrographs in Figures 5.9 and 5.12, the carbon in contact with the high concentration of dissolved oxygen contains a higher density of reduced gold on the carbon surface. This phenomena can be explained electrochemically, which will be handled in the next chapter (Chapter 7).

5.7 Summary

Mixing experiments highlighted that the adsorption of gold-iodide onto activated carbon is controlled by a one step rate controlling mechanism. This is deducted from that the fact that a plot of $\ln(C_s^o/C_s)$ versus time yields a straight line. Furthermore, an interruption test indicated clearly that intra-particle diffusion is minimal or non-existent.

The adsorption curves of change in initial gold concentration gave a strong indication that gold was reduced on the carbon surface and that the reduced gold can have a "blinding" effect.

Meanwhile, the concentration of iodine and iodide in the solution play an important rȯle during the adsorption. The iodine concentration affects the adsorption kinetics and equilibrium point adversely, while, iodide concentration had relatively no effect on the adsorption. It is known that the increase in iodine, leads to an increase in the tri-iodide ion, which is the principal oxidising agent. This leads to the competitive adsorption between the iodine, tri-iodide and the gold-iodide. Further, the tri-iodide can re-dissolve the gold metal from the carbon surface and it also attacks the carbon surface, leading to the degradation thereof.

The pre-treatment of the carbon with iodine/iodide solutions, emphasises the competitive adsorption between the above mentioned ions. The further pre-treatment of the carbon with sodiumthiosulphate, which oxidises all iodine to iodide, thereby depleting the concentration of the tri-iodide, shows that the reaction of the tri-iodide with the carbon surface has actually a negligible effect on the adsorption of the gold complex which is opposite of what would be expected from the oxidising capability of the ion.

The pH level plays an important role in the type of adsorption that occurs, in an alkaline medium, the gold complex tends to reduce to metallic gold on the carbon surface, while in an acidic medium, the ion-exchange mechanism is favoured.

Higher dissolved oxygen concentration favours the reduction of the gold-iodide.

Stirring rate [rpm]	**k_f [m.s^{-5}] x 10^5**
80	2.2
150	4
200	4.1
300	4.3
500	4.7

TABLE 5.1 : Film transfer coefficients at different stirring speeds

Conditions	**k_f [m.s^{-1}] x 10^5**	**A**	**n**
[Au] = 10 ppm	4.3	50	0.25
[Au] = 20 ppm	4.3	60	0.25
[Au] = 30 ppm	4.3	68	0.25
[Au] = 50 ppm	4.3	90	0.25

TABLE 5.2 : Sensitivity of mass transfer parameters - Diffferent initial gold concentrations.

Conditions	**k_f [$m.s^{-1}$] x 10^5**	**A**	**n**
only iodide	4.6	65	0.25
"standard"	4.3	60	0.25
0.01 M I_2 added	3.0	9	0.25
0.02 M I_2 added	3.0	5.5	0.25

TABLE 5.3 : Sensitivity of mass transfer parameters - Different I^-/I_2 concentrations

Conditions	**k_f [m.s^{-1}] x 10^5**	**A**	**n**
pH 1.5	4.3	75	0.25
pH 6.5	4.3	60	0.25
pH 11	4.3	70	0.25

TABLE 5.4 : Sensitivity of mass transfer parameters : Different pH levels.

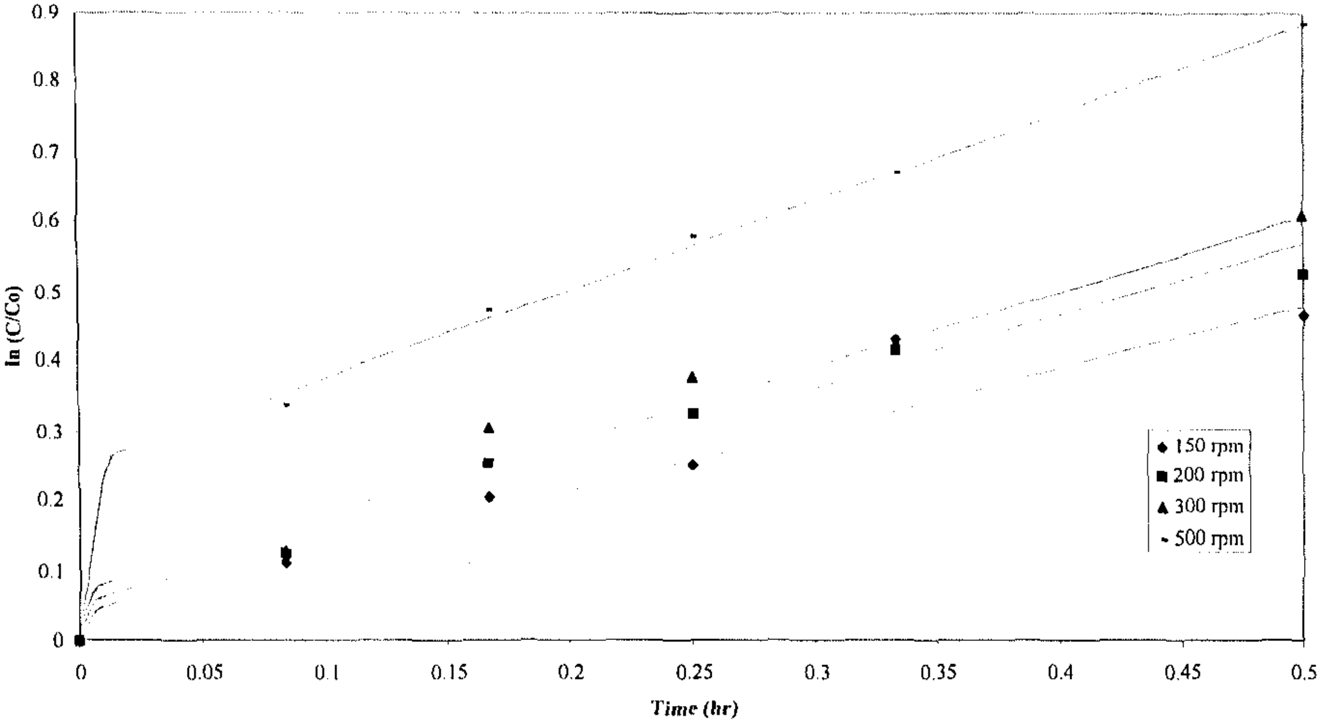


FIGURE 5.1 : Logarithm of (C_0/C) versus Time (C_0 = 20 ppm, m = 1g)

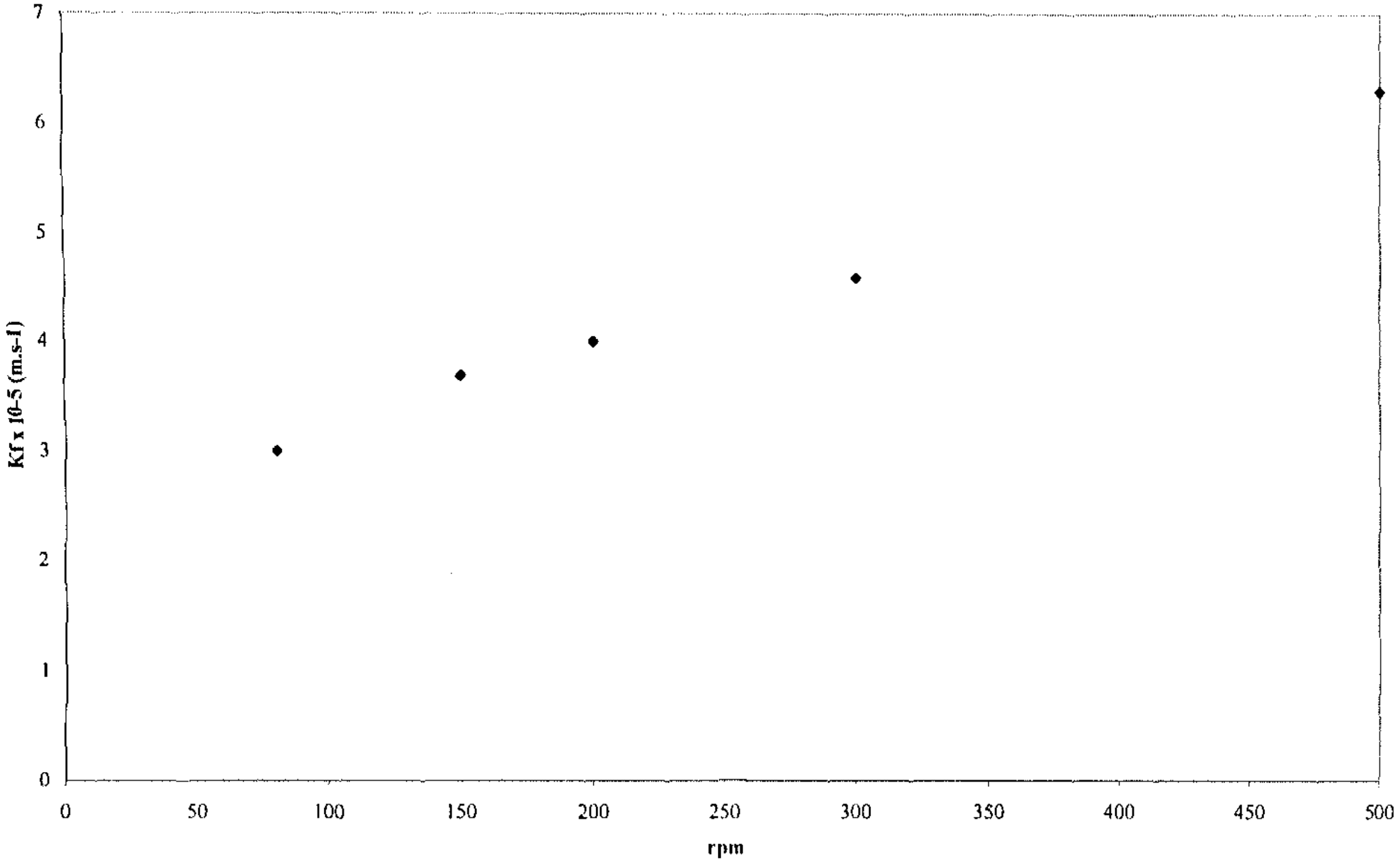


FIGURE 5.2 : Film transfer coefficient (k_f) as a function of stirring speed for gold-iodide in a batch reactor.

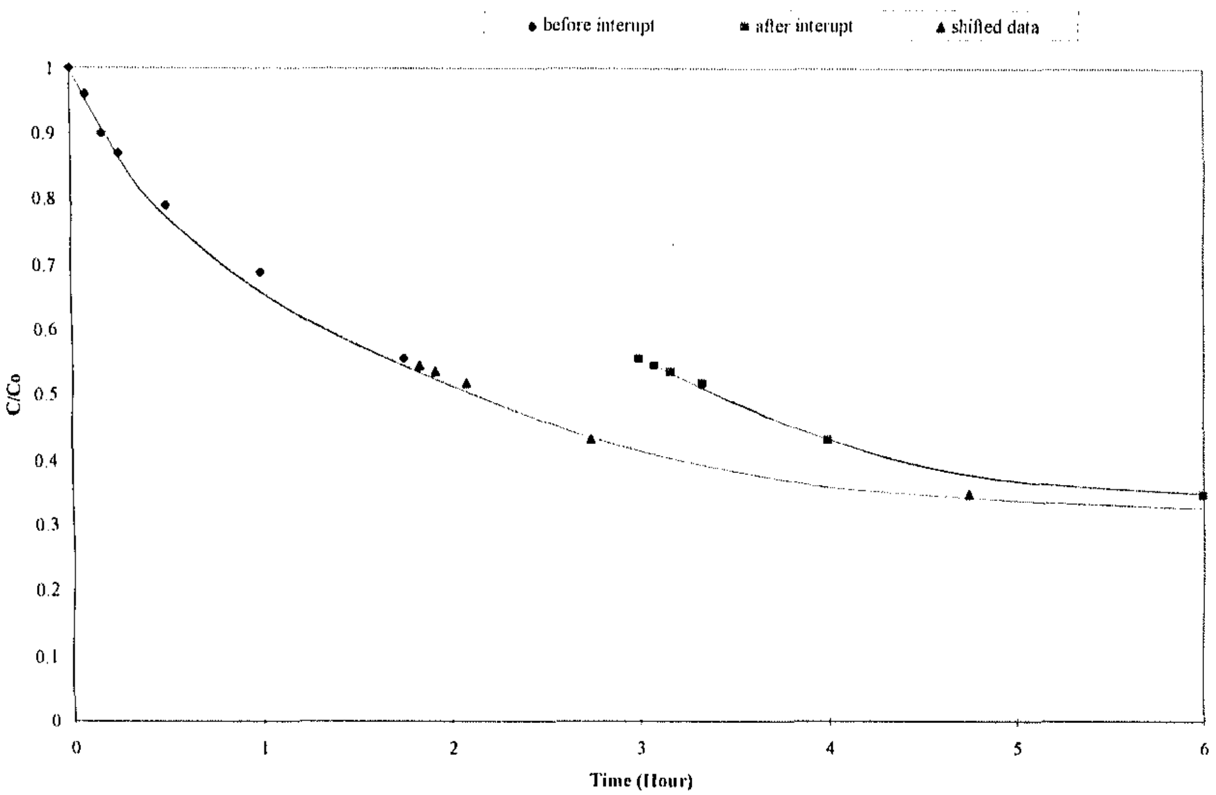


FIGURE 5.3 : Effect of interruption on adsorption profile of gold-iodide onto activated carbon. (C_c^0 = 20 ppm; m_c = 0.5 g; N = 300 rpm; pH = 6.5; V_s = 1 L)

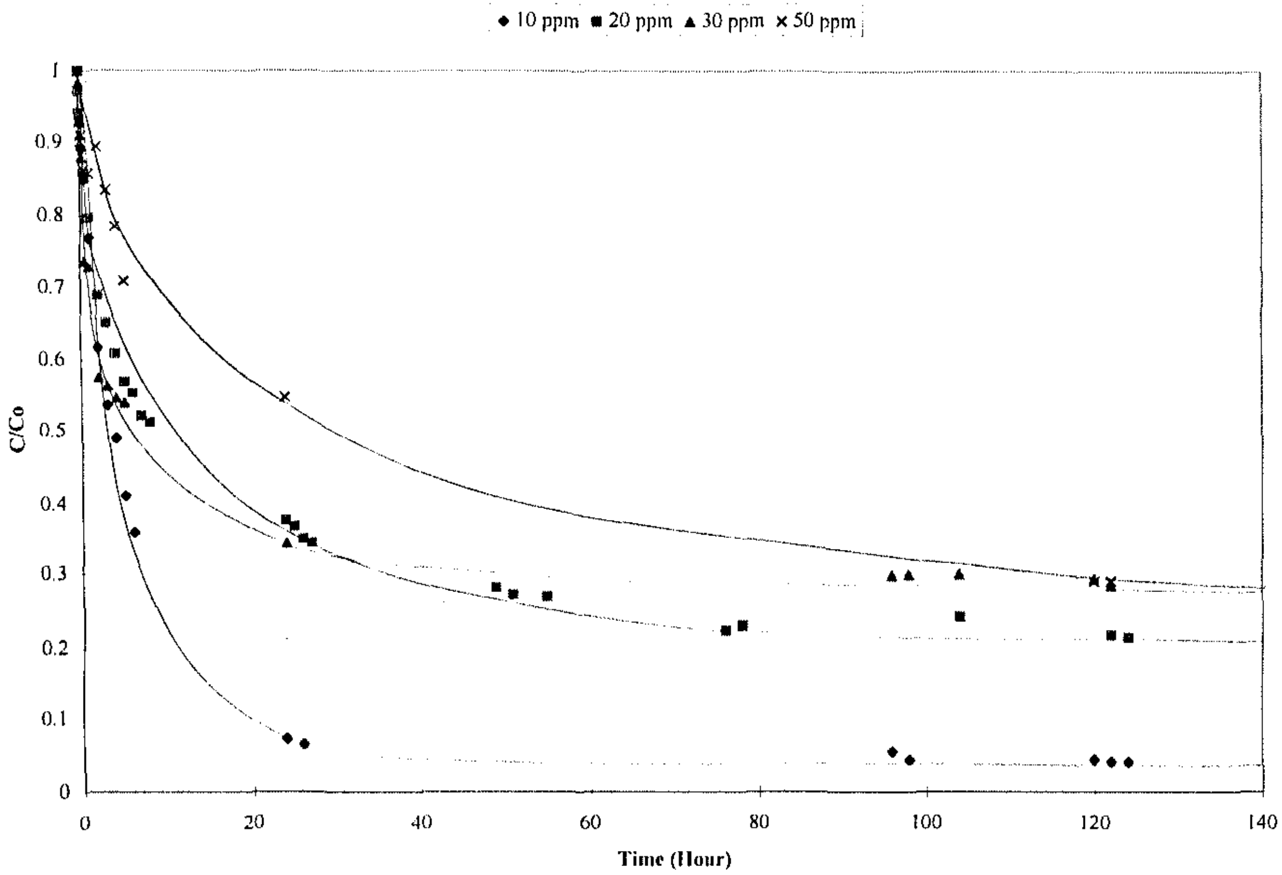


FIGURE 5.4 : Adsorption profile of gold-iodide onto activated carbon at different initial gold-iodide concentrations.(m_c = 0.2 g; N = 300 rpm; pH = 6.5; V_s = 1 L)

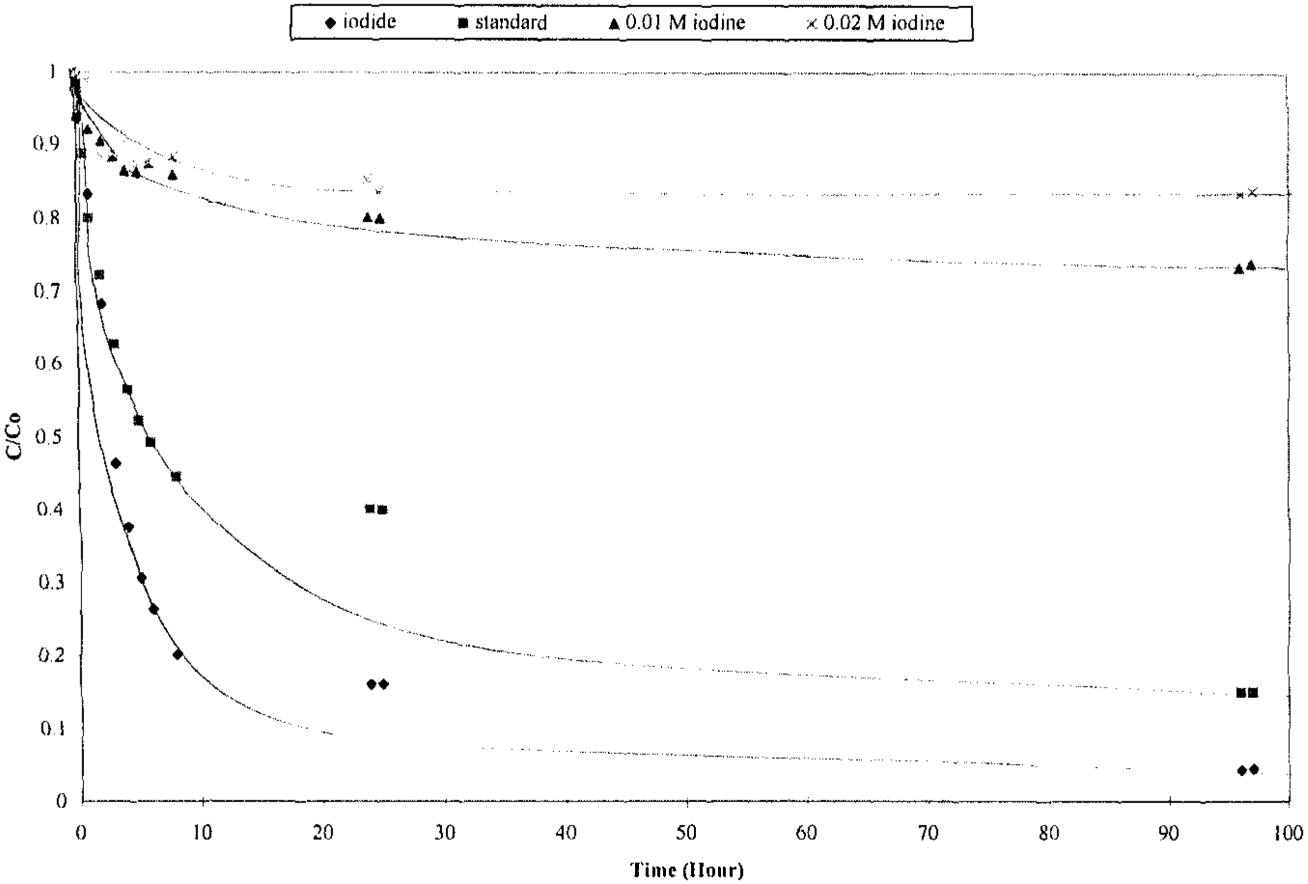
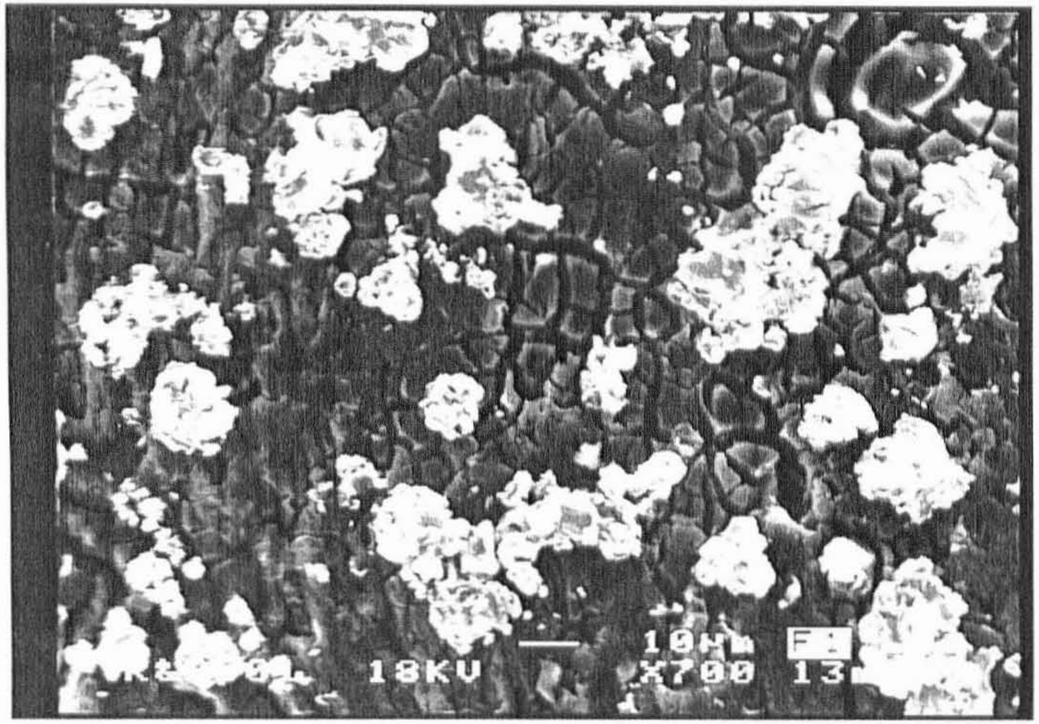


FIGURE 5.5 : Adsorption profile of gold-iodide onto activated carbon at different concentrations of iodine, iodide and tri-iodide. (C_c^o = 20 ppm; m_c = 0.2 g; N = 300 rpm; pH = 6.5; V_s = 1 L)



FIFURE 5.6 : Electron scanning micrograph of activated carbon surface after 48 hr contact with 200 ppm gold-iodide and 0.2 M I2 and 0.2 M I- solution at pH 6.5 (magnification X700)

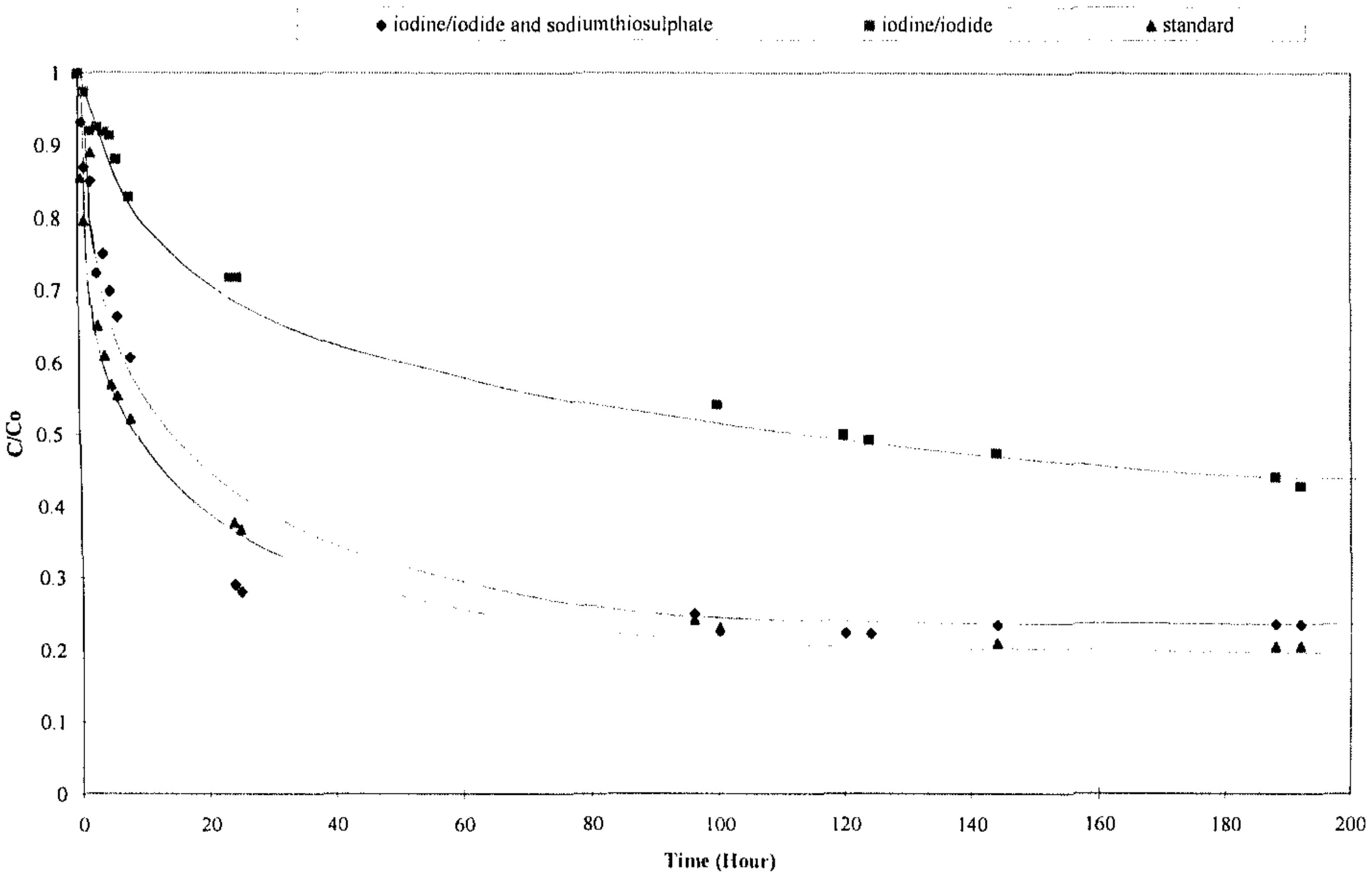


FIGURE 5.7 : Adsorption profile of gold-iodide onto activated carbon showing the influence of pretreatment of carbon with iodine/iodide solution.

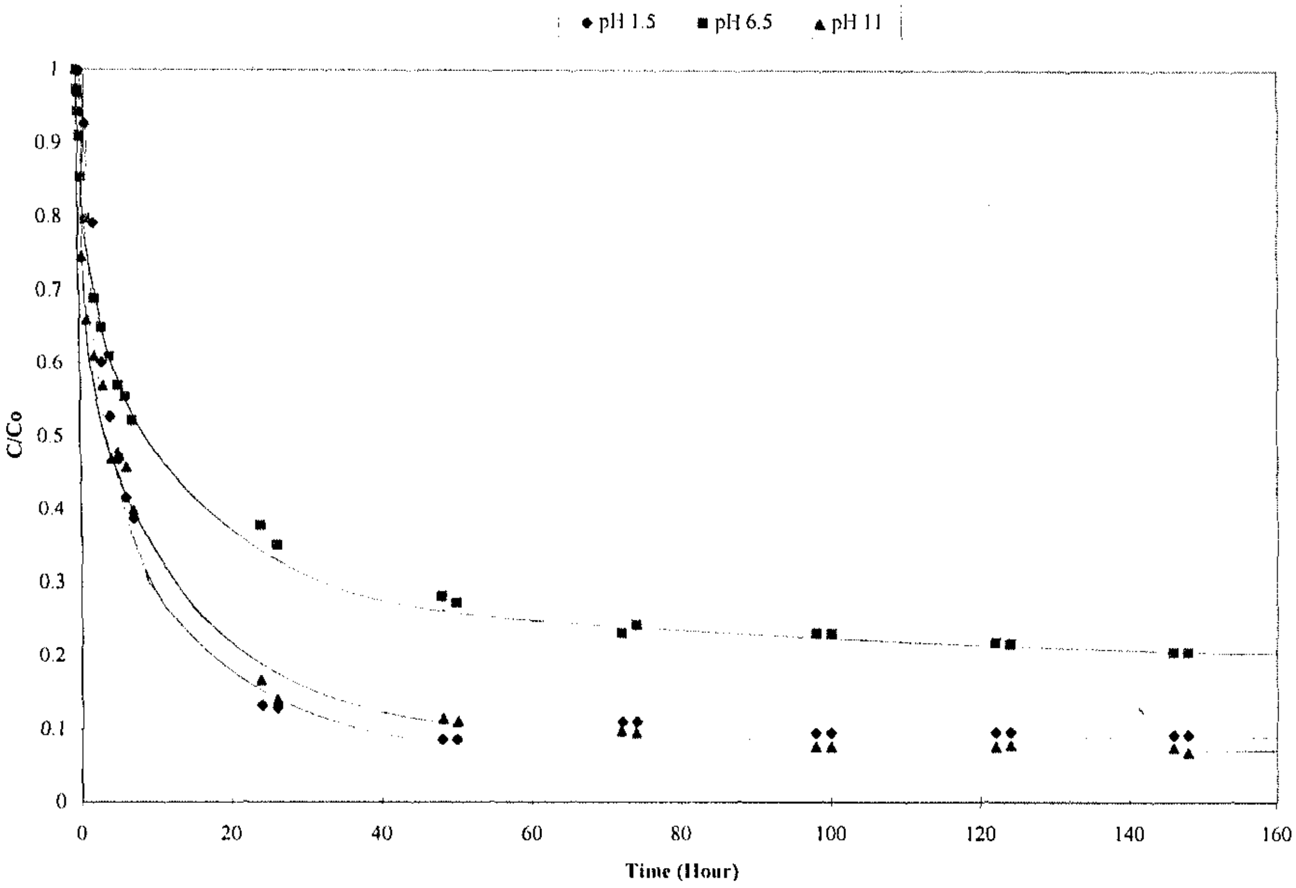


FIGURE 5.8 : Adsorption profile of gold-iodide onto activated carbon at different pH levels. ($C_c^0 = 20$ ppm; $m_c = 1$ g; N = 300 rpm; $V_s =$ 1 L)

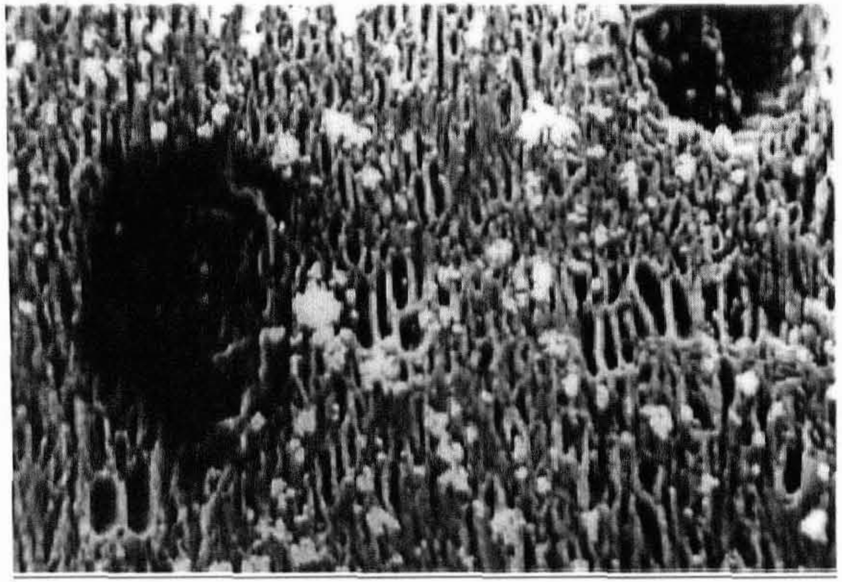


FIGURE 5.9 : Electron scanning micrograph of activated carbon surface after 2 weeks contact with 20 ppm. gold-iodide solution at pH 6.5 (magnification x 1000)

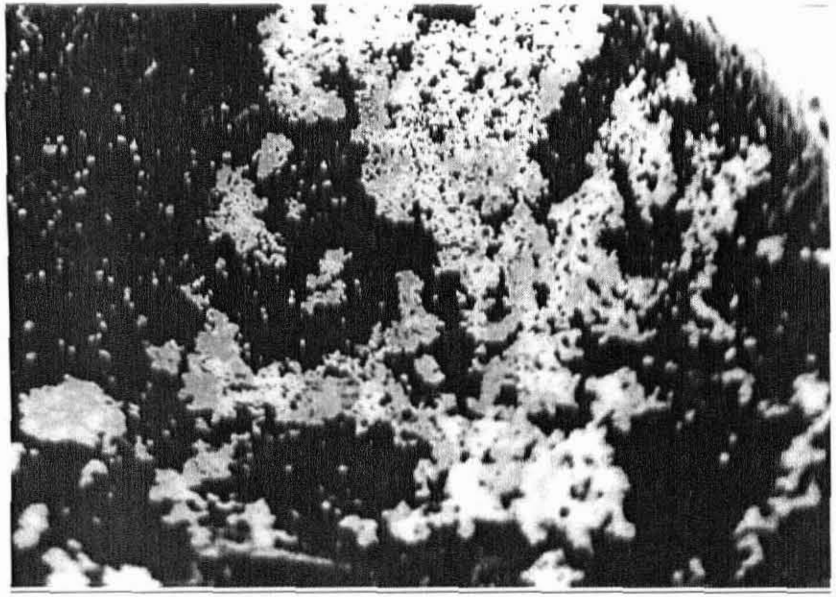


FIGURE 5.10 : Electron scanning micrograph of activated carbon surface after 2 weeks contact with 20 ppm. gold-iodide solution at pH 11 (x 100 magnification)

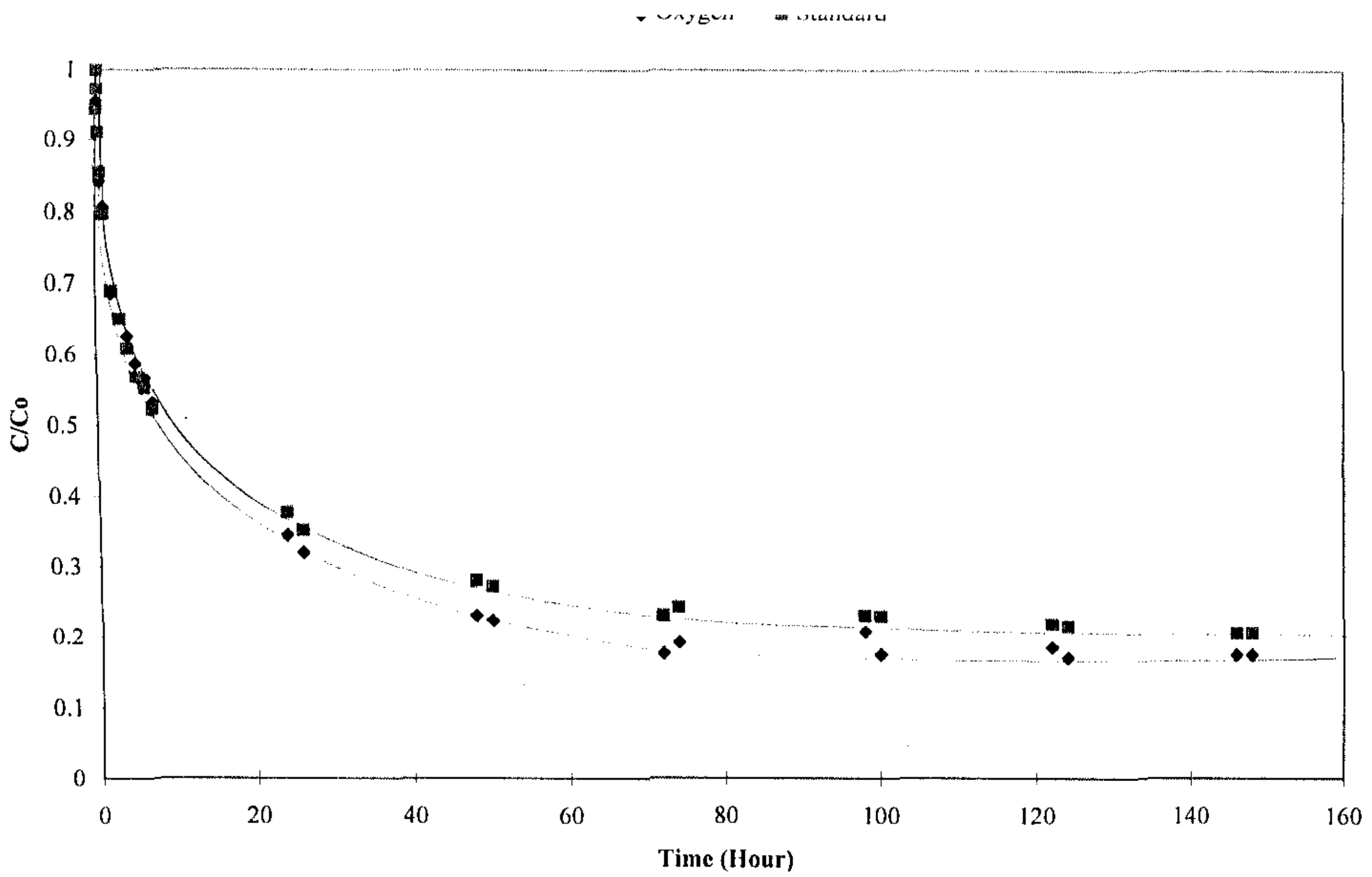


FIGURE 5.11 : Adsorption profile of gold-iodide onto activated carbon at different concentrations of dissolved oxygen (C_c^o = 20 ppm; m_c = 1 g; N = 300 rpm; V_s = 1 L)

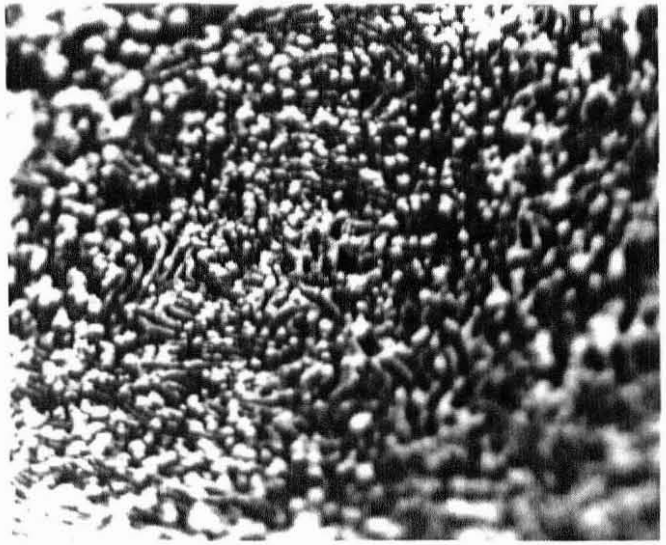


FIGURE 5.12 : Electron scanning micrograph of activated carbon surface after two weeks contact with 20 ppm. gold-iodide solution at pH 6.5 and[dissolved oxygen] = 32 ppm. (magnification x 100)

CHAPTER 6

BASIC ELECTROCHEMICAL APPROACH

In this chapter, the effect of the potential of both the gold-iodide solution and the activated carbon surface on the adsorption characteristics and nature of the gold onto the activated carbon was investigated. Some experiments performed in Chapter 5 were repeated, except, that the potential of the solution was measured by a platinum electrode versus a standard calomel (3 M KCl) reference electrode (SCE). The potential of the carbon was measured by using a polished glassy carbon electrode versus the same SCE. According to Marsh (1994), a polished glassy carbon electrode has similar functional groups on the surface to activated carbon, and therefore this electrode is used as a guide for the potential on the activated carbon surface.

6.1 SOLUTION AND CARBON POTENTIALS

6.1.1 EFFECT ON IODINE / IODIDE SYSTEM

Previous studies performed on the adsorption of gold complexes onto activated carbon, have focused primarily on the mechanism of mass transfer and the physical adsorption of the ions onto the carbon surface. However, the role of the species present in the solutions, is detrimental to the activity of the carbon, and hence these species affect the adsorbed gold complexes.

Therefore, to explain the influence of the iodine, iodide and tri-iodide ions on the adsorption of gold-iodide onto activated carbon, the species present in the solution must be investigated. This was done by using the Pourbaix diagram (Figure 6.1) for the iodine/iodide - water system (Kelsall *et al,* 1992). This diagram shows clearly the areas where each species is dominant. The readings of the solution potentials (E values) at different pH levels (Table 6.1) were superimposed onto this diagram and show which species are dominant in solution.

It can be seen, that at pH of 2, the experiment starts in the region where we have iodine as the dominant species, whereas at the end of the adsorption experiment, the solution potential lies in the tri-iodide area. This can explain why metallic gold is not readily seen at the carbon surface. The presence of tri-iodide ions, which is a strong oxidising ion, re-dissolves most of the gold reduced from the carbon surface and enhances thereby the ion-exchange mechanism, instead of reduction. Meanwhile, at a pH level of 6.5, which is the “ standard” solution, the solution potential drops into, the area where the iodide is prevalent. Therefore, gold can be found on the carbon surface in metallic form or in an ionic form. At pH of 11, the dominant species throughout the experiment are iodate and iodide, which will not inhibit the reduction of the gold complex onto the carbon surface, nor will it re-dissolve the reduced gold present on the carbon surface.

6.1.2 POTENTIAL OF THE CARBON

Combining the E-values obtained, with the Eh-pH diagram for gold iodide complexes (Kelsall *et al*, 1992), resulted in Figure 6.2. This clearly indicates the nature of the gold species which are dominant in the solution. At pH level of 2 and 6.5, the gold iodide is mainly in its ionic form, while at pH of 11, after 2 hr of contact with gold-iodide, the potential on the glassy carbon electrode falls in the metallic gold area, which will induce the reduction of the gold complex on the carbon surface.

6.2 ELECTROCHEMICAL CONSIDERATIONS

The electrochemistry involved in the reduction of the gold-iodide complex is combined in the following set of reactions:

$AuI_4^- + 3e^- \Leftrightarrow Au + 4I^-$ $E_o = 0.57$ V (6.1)

$AuI_2^- + e^- \Leftrightarrow Au + 2I^-$ $E_o = 0.57$ V (6.2)

$CO_2 + 4H^+ + 4e^- \Leftrightarrow C + 2H_2O$ E_c (6.3)

$4AuI_4^- + 3C + 6H_2O \Rightarrow 4Au + 3CO_2 + 12H^+ + 16I^-$ (6.4)

$4AuI_2^- + C + 2H_2O \Rightarrow 4Au + CO_2 + 4H^+ + 8I^-$ (6.5)

The E_o values for equations 6.1 and 6.2 were obtained from Hiskey and Atluri (1988). The carbon (C) in Equation 6.3, is a generic assumption. There are various functional groups and active sites on the carbon surface, which will form an reduction / oxidation reaction with the gold-iodide.

For reduction/cementation of the gold complex to take place, the result of Equation 6.6 must be negative :

$$E_o - E_c = \Delta E \qquad (6.6)$$

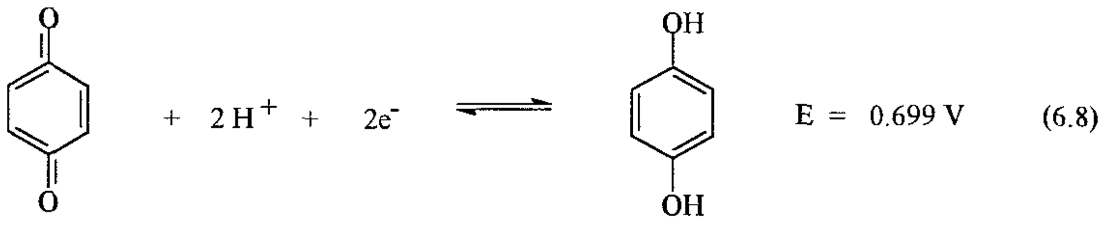
Adsorption tests conducted at pH of 11, the pH of the solution decreased rapidly to a level of approximately 8. This substantiates Equations 6.4 and 6.5, where H^+ ions are a by-product of the reduction of the gold complex.

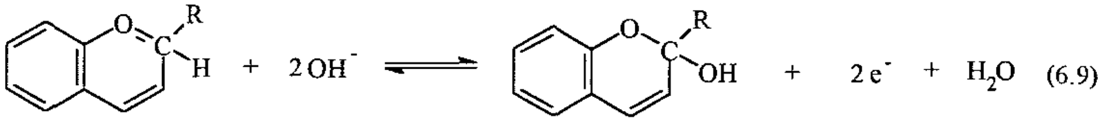
Jankowska *et al* (1980) investigated the electrochemical properties of activated carbon in halide solutions and concluded that the potential of the activated carbon is relative to the type of anion species present in the solution. This effect on the activated carbon potential, was the strongest for solutions containing iodide ions, bringing the potential of the carbon down.

Furthermore, the carbon potential, E_o, is dependent on the pH of the solution. Thus, the Nerst equation for Reaction 6.3 can be modified as follows :

$$E = E_o - 0.059.\mathrm{pH} \quad (V) \qquad \text{for } T = 25^\circ C \qquad (6.7)$$

Also, some of the groups identified (Adams, 1990) on the carbon surface are quinone and the chromene groups (Reactions 6.8 and 6.9). These can oxidise and form the couple with the gold-iodide reducing the latter to elemental gold.





As explained in the previous chapter (Chapter 5), dissolved oxygen enhances the reduction of the gold-iodide. This can be explained by the oxidation of the adsorbed oxygen on the carbon surface by the following reaction :

$$O_{2\,(ads)} + 2H_2O + 4e^- \Leftrightarrow 4\,OH^- \qquad E_o = 0.401\text{ V} \qquad (6.10)$$

This leads to an increase of pH, thereby creating an region where gold-iodide is more readily reduced. As most of the active sites on the carbon surface are not quantified as yet, it can be assumed that other sites can also act as an electrochemical couple.

Time	**pH 2**		**pH 6.5**		**pH 11**	
Days	**G.C.**	**Pt**	**G.C.**	**Pt**	**G.C.**	**Pt**
0	636.5	636.5	640.5	641.5	550.5	no readings taken
0.3	615.5	617.5	617.5	620.5	488.5	
1	571.5	633.5	491.5	587.5	399.5	
2	571.5	581.5	486.5	574.5	353.5	
3	567.5	582.5	477.5	569.5	341.5	
4	567.5	581.5	472.5	569.5	271.5	
5	567.5	582.5	472.5	569.5	271	
6					269.5	
7					271.5	
8					271	

TABLE 6.1 : potential of gold-iodide solution at different pH levels - saturated calomel (Kcl) vs. platinum or glassy carbon (G.C) electrode

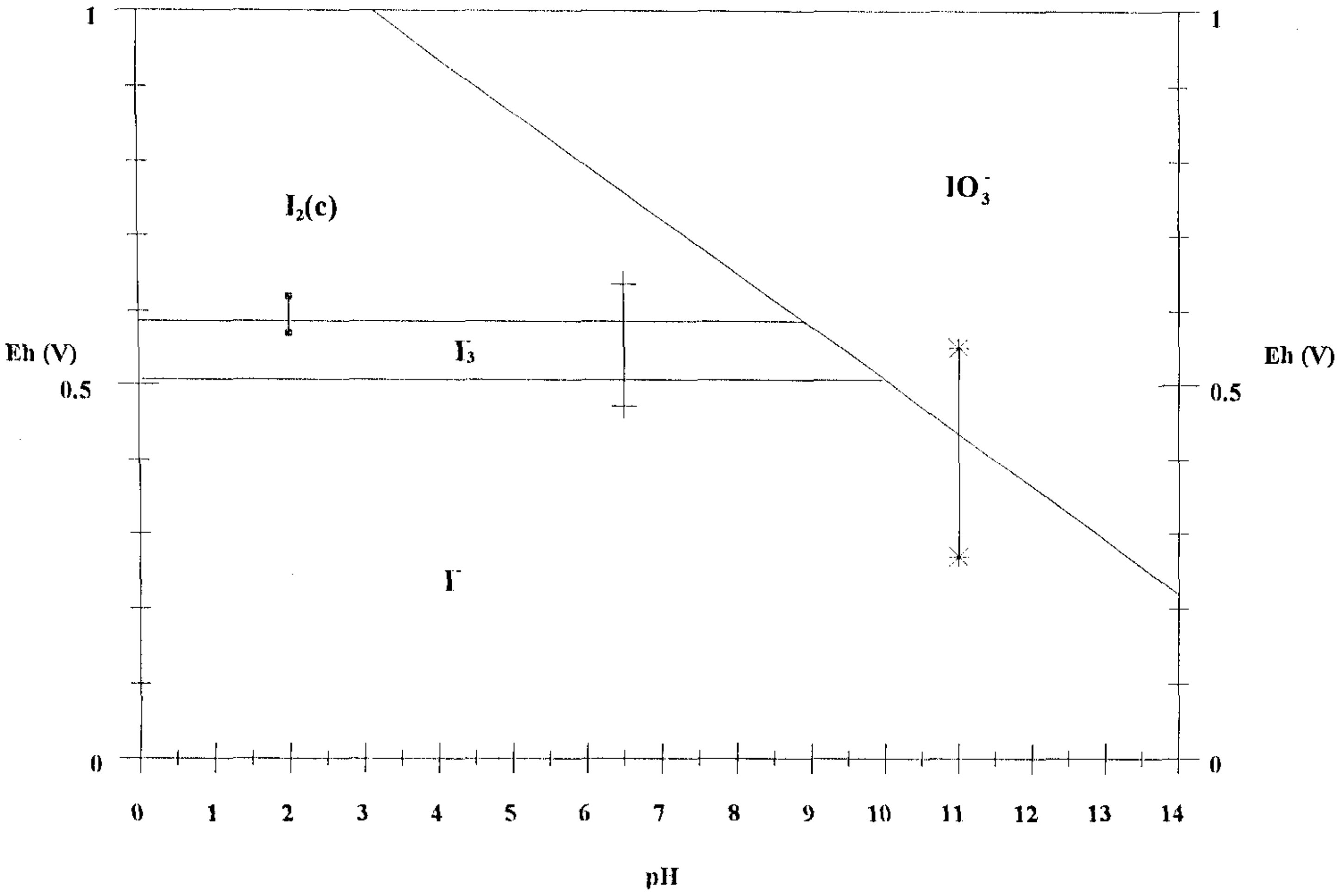


FIGURE 6.1 : Eh-pH equilibrium diagram for iodide/water system $[I^-] = 1$ M

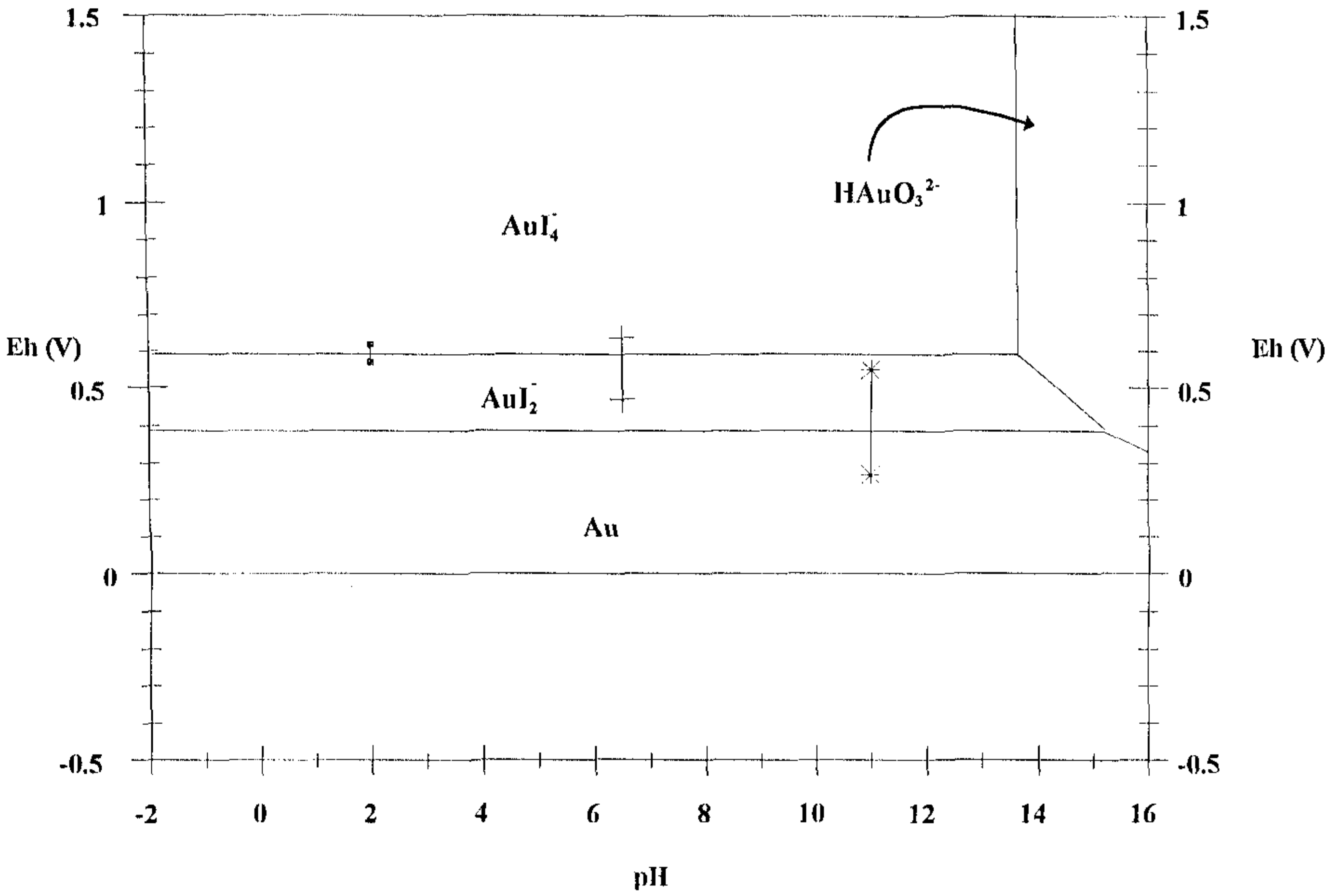


FIGURE 6.2 : Eh-pH equilibrium diagram for gold-iodide/water system [Au] = 10^{-5} and [I$^-$] = 1 M

CHAPTER 7

CONCLUSIONS
AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following conclusions were drawn from this study :

a) Adsorption was found to be rate limited by a first order film diffusion mechanism.

b) At different initial gold concentrations, the adsorption kinetics and equilibrium for gold-iodide was lower at higher concentrations. The reason for this is that the gold complex partially reduces onto the carbon surface, thereby shielding and eliminating active sites for further adsorption.

c) In the case where the initial concentrations for iodine/iodide were changed, the effect of the principal oxidising agent, namely the tri-iodide ion, became dominant. In the case where only iodide was present in solution (thereby eliminating the tri-iodide) the adsorption kinetics was fast, compared to solutions containing iodine. In these solutions, the presence of the tri-iodide gave rise to the re-dissolution of the gold from the carbon surface. Furthermore, tri-iodide and iodine are also adsorbed by activated carbon, thereby creating a competitive adsorption between these elements. Further experiments, where the activated carbon was pre-treated in iodine/iodide solutions, shows clearly that where all the iodine was reduced to iodide by treatment with sodiumthiosulphate, the adsorption kinetics and equilibrium were much faster and higher then the case were the iodine was left on the carbon surface.

d) In an acidic medium, the gold tends to be adsorbed by ion-exchange and/or physisorption. The proposed principle behind this is that in an acidic solution the prominent iodine species are in the form of iodine and tri-iodide.

e) Meanwhile, in an alkaline solution, only iodine and iodate are present. Therefore, the gold present on the surface of the carbon remains in its reduced form. Thereby, the gold complex on the carbon surface is found in two states, namely in its ionic form and as metallic gold.

f) Dissolved oxygen adsorbed on the activated carbon, leads to the reduction of oxygen and water to hydroxide ions, thereby increasing the alkalinity of the surrounding liquid film and hence decreasing the concentration of the oxidising agent, the tri-iodide ion.

g) Approaching the adsorption of gold-iodide from a basic electrochemical approach, we can deduct by measuring the approximate potential of the activated carbon and using Porbaux diagrams for the gold-iodide/water and iodine-iodide/water systems that in acidic medium the predominant gold species tends to be gold-iodide and for iodine species, the tri-iodide ion predominates, substantiating the deductions made in the a previous paragraph.

h) In an alkaline medium, the predominant gold species tends to be metallic gold and for iodine, the iodate and iodide ion. Also, the alkaline medium favours the oxidation of functional groups on the carbon surface, thereby promoting a electrochemical couple between the gold complex and the carbon surface.

7.2 RECOMMENDATIONS

a) In order to fully elucidate the mechanism of gold-iodide adsorption onto activated carbon, future work is necessary to investigate the reduction phenomenon of gold-iodide onto the carbon surface.

b) A complete electrochemical study needs to be performed to quantify this phenomenon.

c) The interaction between the carbon, iodine, iodide and tri-iodide need to be investigated so as to quantify their individual effects on the overall performance of gold adsorption

d) The adsorption of gold-iodide onto ion-exchange resins need to be investigated.

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NOMENCLATURE

A	parameter in Freundlich isotherm
A_c	effective external surface of carbon [m^2]
C_c^e	equilibrium gold loading on carbon surface [$mg.g^{-1}$]
C_c^e	gold loading on carbon [$mg.g^{-1}$ carbon]
C_c^o	initial gold loading on carbon surface [$mg.g^{-1}$]
C_s	solution concentration [$mg.l^{-1}$]
C_s^e	equilibrium solution concentration [$mg.l^{-1}$]
C_s^o	initial solution concentration [$mg.l^{-1}$]
d_p	average carbon particle diameter [m]
E	approximate potential of activated carbon
E_c	half cell potential for activated carbon functional group
E_0	half cell reaction potential
k_f	external film transfer coefficient [$m.s^{-1}$]
m_c	mass of carbon [kg]
m_s	mass of solution [kg]
n	empirical constant in Freundlich isotherm
ρ	apparent density of carbon [$kg.m^{-3}$]
V_s	volume of solution [m^3]

APPENDIX A

SOLUTION OF FILM DIFFUSION MODEL

This programme solves Equation 3.12. The program was written in Turbo Pascal version 4.0 and the output is in the form of a graph of solute concentration versus time.

STRUCTURE OF MAIN PROGRAMME

The programme starts by setting the concentration equal to the initial concentration. Equation 4.12 is then solved using a fourth-order Runge-Kutta routine, producing a concentration versus time curve.

The following nomenclature was used:

PROGRAMME	**THESIS**	**PROGRAMME**	**THESIS**
co	C_s^o	Qs	Q_s
cs	C_c	kf	k_f
ct	C_s		
dp	d_p		
p	r		

```
program runge_kutta;

uses
   Crt,grafiek;

var
  D : text;
  g,ron : integer;
  inc,a,b,c,e,ct,time,z,f,cs,n,ro,co,v,m,kf,p,dp,qs : real;
  q : string;

    procedure test;

   begin
   qs:=((v/m)*(co-ct))+0.0000001;
   cs:=xmagy(qs/e,1/n);
   f:=((6*kf*m)/(p*dp*v))*(cs-ct);
   end;

   procedure  calculation;

   begin
   a := f * inc;
   time := time + (inc/2);
   ct := z + (a/2);
   test;
   b := f * inc;
   ct := z + (b/2);
   test;
   ct := f * inc;
   time := time + inc/2;
   ct := z + c;
   test;
   ct := z + (a + 2*(b + c) + inc * f)/6;
   z := ct;
   end;



begin

  ClrScr;
  textcolor(14);
  Writeln('This program solves a combined differential and algerbraic');
  Writeln('equation using the Runge-Kutta method');

  {Writeln('Solving a differential equation by Runge-kutta method');}
  Writeln('--------------------------------------------');
  Writeln('please give the name and the path of the answer file');
  readln(q);
```

```
   {writeln('what is the increment');
   readln(inc)}
   inc := 0.1;
   {write('input inital value of x(0)..  ');
   readln(time);}
   time := 0;
   {write('input inital value of y(0)..  ');
   readln(z);}
   Writeln('What is initial concentration in ppm e.g. 100ppm');
   readln(co);
   z := co;
   writeln('what is the value of A ');
   readln(e);
   writeln('what is the value of n');
   readln(n);
   writeln('what is the value of M');
   readln(m);
   writeln('what is the value of V');
   readln(v);
   writeln('what is the value of P');
   readln(p);
   writeln('what is the value of dp');
   readln(dp);
   writeln('what is the value of kf');
   readln(kf);
   {writeln('results');}
   Assign(D, q);
   rewrite(D);
   for g := 1 to 2000 do begin
   ct := z;
   calculation;
   {ver :=  time*10;}
   ron := round(time*10);
   ro := ron/10;
   if frac(ro) = 0 then begin;
   writeln(time:0:4,'   ',ct:0:8);
   writeln(D, time:0:4,'   ',ct:0:8);
   end;

   end;

   close(D);
   Writeln('The answer values are now stored at/under');
   writeln(q);
   writeln('wait');
   delay(5000);
end.
```

APPENDIX B

PUBLICATIONS FROM THESIS

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1. P.A.M. Teirlinck and F.W. Petersen - The adsorption of gold from iodide solutions onto activated carbon, *Conference Proceedings, 7th National Meeting of the South African Institution of Chemical Engineers*, Johannesburg, pp. 74 - 98, (1994)
2. Teirlinck, P.A.M., Petersen, F.W. Factors influencing the adsorption of gold-iodide onto activated carbon. *Sep. Sc. and Techn.*, **30**(16), pp 3129-3142 (1995)
3. Teirlinck, P.A.M., Petersen, F.W. The nature of gold-iodide adsorption onto coconut-shell type carbon. *Minerals Engineering*, **9**, No. 9 , pp. 923-930 (1996)

THE ADSORPTION OF GOLD FROM IODIDE SOLUTIONS ONTO ACTIVATED CARBON

by

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ABSTRACT

Activated carbon has been used extensively in the mining industry to extract gold from cyanided pulps. However, in recent years considerable attention has been given to so-called safer technology with the substitution of cyanide by halogens such as bromide, chloride and iodide. It is the aim of this paper to investigate the adsorption of gold-iodide onto a coconut shell activated carbon. Equilibrium loadings on the carbon showed clearly that gold-iodide has a higher loading profile than gold cyanide. Furthermore, pH, the effects of iodide concentration and level of dissolved oxygen have little or no influence on the kinetic and equilibrium parameters in a film diffusion model. However, the initial concentrations of gold-iodide, iodine and tri-iodide significantly influenced both the rate and equilibrium of gold-iodide adsorption. Scanning electron microscopy showed that the gold-iodide complex is reduced to metallic gold on the surface of the carbon. This is also manifested in the high film transfer coefficients obtained for gold iodide adsorption.

INTRODUCTION

With increasing environmental legislation, it becomes more important to industry to explore methods whereby existing processes can be optimized in terms of safety and health. The carbon-in-pulp (CIP) process is the preferred method of extracting gold from leached pulps. Currently, the pulp is being leached with potassium cyanide so as to dissolve the gold. The major concerns with the use of cyanide is the formation of deadly hydrogen cyanide gas, the adsorption through the skin and accidental ingestion of cyanide salts. Formation of cyanide complexes with organic and inorganic substances, which are difficult to destroy by conventional methods can, with other free forms of cyanide, contaminate effluent streams and so create a dangerous situation at the tailings dams. Therefore, a need exists to investigate alternative lixiviants for gold adsorption.

Previous studies (1,2,3,4) have showed that gold leached readily in a relative dilute iodine/iodide solution. Qi and Hiskey (3) stated that the dissolution rate of gold in an iodine/iodide solution is the same as for cyanide solutions, thus indicating that the dissolution rate of iodide can be as effective as cyanide in the leaching process. Furthermore, it is well known that the gold-iodide complex is the most stable of the halogen group at room temperature (1).

Hughes and Linge (5) investigated the adsorption kinetics of gold chloride on activated carbon and came to the conclusion that the rate controlling step was mass transfer over the film boundary which they characterised with a first order rate constant. The rate constant was independent of the initial gold concentration in the solution. They further stated that the rate was controlled by a surface reaction which becomes increasingly more important by stirring, and hence gradually changes from pure mass control to mixed control of the reaction. Sun and Yen (6) observed that the concentration of the chloride- and hydrogen ions (acidity) did not play a role in the adsorption rate as activated carbon has a very low affinity towards the chloride ion. On the other hand, dissolved chlorine decreased the rate of gold adsorption probably due to the re-dissolution of the gold from the carbon surface by aqueous chlorine.

Hiskey and Qi (7) investigated the uptake of gold onto activated carbon from iodide solutions. They found that the gold complex reduces to fine gold particles on the surface of the carbon and extremely small particles inside the pore structure of the carbon matrix. However, it is not clear whether the presence of small gold particles inside the carbon's matrix could be attributed to partial intra-particle diffusion.

This paper will investigate factors influencing the adsorption of gold-iodide onto activated carbon . Furthermore the kinetic and equilibrium parameters in a film diffusion model will be used to evaluate the sensitivity in the factors influencing gold adsorption from an iodide solution.

THEORY

Equilibrium constants

The Freundlich isotherm (Eq. 1) fitted the equilibrium curves for the adsorption of gold-iodide onto activated carbon. The values for *A* and *n* were obtained by drawing a graph of ln C_c^e against ln C_s^e. A straight line is produced of slope *n* and intercept ln *A*. The parameters *A* and *n* are compared in Table 1 to values obtained from gold cyanide equilibrium data.

$$C_c^e = A(C_s^e)^n \tag{1}$$

Mass transfer coefficient

Johns (8) derived a model for the adsorption of gold cyanide onto activated carbon. This model expresses an equation (Eq. 2) which derives the gold concentration in solution at any time in a batch reactor. The following assumptions were made in developing the model :

- inter-diffusion is treated as quasi-stationary.
- diffusion across the film is fast compared to the concentration changes at the film boundary.
- The film is treated as a planar layer (one dimensional diffusion).
- The particles can be treated as equivalent spheres with a homogeneous outer surface.

A computer program was written to obtain the k_f values (Table 3) for the adsorption curves.

$$\frac{dC_s}{dt} = -k_f(\frac{A_c}{V_s})C_s + k_f(\frac{A_c}{V_s})A[C_c^o + (\frac{m_s}{m_c})C_s^o + (\frac{m_s}{m_c})C_s]^{n} \qquad (2)$$

EXPERIMENTAL

All experiments were performed in a 1 L baffled batch reactor. Agitation was provided by a flat blade impeller, driven by a Heidolph variable speed motor. The impeller speed was kept constant at 300 rpm except for experiments performed in the determination of the film transfer coefficient. Fine gold nuggets (1 g) were dissolved in a 1 L volumetric flask using 0.1 M KI and 5×10^{-3} M I_2 to obtain a 1000 ppm Au solution. All reagents used were of analytical grade and distilled water was used throughout. The pH was adjusted using either a 1 M HCl or 1 M KOH solution and was measured with a Beckmann Φ71 pH meter. The nitrogen and oxygen gases were supplied by Fedgas and the dissolved oxygen levels were measure with a Hanna HI 8043 dissolved oxygen meter. All experiments were performed at room temperature.

Samples were taken at regular intervals and the gold concentration was measured using a Varian AA-1275 atomic adsorption spectrophotometer. The concentrations of I_2 and I^- were obtained by titration against $Na_2S_2O_3$ and KIO_3 respectively. A coconut shell activated carbon (average diameter of 1.4 mm) provided by ACIX was used as an adsorbent. Initially, 1 g of carbon was used but due to the rapid drop in gold-iodide concentration to almost 0 ppm in the reactor, it was decided to decrease the mass of carbon to 0.2 g. Equilibrium tests were performed over a period of three weeks.

RESULTS AND DISCUSSION

Adsorption experiments with gold-iodide were used to evaluate kinetic and equilibrium parameters in the film diffusion model. These parameters will be discussed qualitatively for each of the factors influencing gold-iodide adsorption.

Mixing

The stirring rate influences the rate of mass transfer of gold-iodide from the solution to the carbon surface. The reason behind this is that the increase in stirring speed decreases the diffusion layer thickness surrounding the carbon particle. This decrease in thickness will decrease the film diffusion coefficient (k_f) if a film diffusion mechanism is present.

Initially, the purpose was to define the driving mechanism behind the adsorption of the gold iodide complex. From a preliminary test it was seen that the gold concentration dropped relatively fast versus the same experiment using gold cyanide. This was a first indication that film diffusion might play a pivotal role in the adsorption mechanism. Adsorption tests were performed at five different stirring speeds with samples taken at regular intervals for the first 30 min. with an initial gold concentration of 20 ppm for all the experiments. As explained by Van Deventer (9) a plot of $\ln(C_s^o/C_s)$ versus time yields a straight line that passes through the origin, and the k_f value can be determined from the slope of this line (Equation 3).

$$\ln(\frac{C_s^o}{C_s}) = \frac{6k_f\, m_c}{\rho d_p V_s} t \quad , \qquad as \quad t \rightarrow 0 \tag{3}$$

Figure 1 shows a plot of the coefficients (Table 1) obtained for both gold-iodide and gold cyanide against the impeller speed. While the curve for gold cyanide plateaus off due to intra-particle diffusion taking over from film diffusion, the curve for the gold-iodide yields a straight line indicating that film diffusion remains the primary mechanism of mass transfer.

An interruption test is an useful method for differentiating between intra-particle diffusion and film diffusion. The carbon was separated from the solution for 1.5 hours. If any intra-particle diffusion has taken place, this separation time would allow mass transfer to continue in the carbon pores. The gold-iodide would diffuse further into the pores, thus creating a higher driving force for mass transfer immediately after the re-immersion of the carbon in the solution. As seen from Figure 2 it is clear that no increase in kinetics takes place after the re-addition of the carbon to the solution. This means that film diffusion is the prominent mechanism in operation.

Equilibrium Studies

Equilibrium experiments were performed with different initial concentrations for both gold cyanide and gold-iodide. As seen from Figure 3 and Table 2, the equilibrium loading of the carbon for the gold-iodide is higher than the equilibrium loading for the gold cyanide. This can be explained through the fact that the gold-iodide complex is reduced to metallic gold and hence (see Figure 4) accumulating on the carbon surface, whereas in the case of gold cyanide, diffusion into the carbon particle can take place.

pH

Adsorption tests were performed at three (3) different pH's, namely 4, 6.5 and 10. The potential-pH equilibrium diagram for gold-iodide system illustrates that the AuI_2^- complex is soluble up to a pH of 12. Figure 5 shows clearly that pH does not play a role in the adsorption rate, nor does it change the equilibrium loading of gold-iodide for the conditions set out in the figure caption.

At a solution pH of 10 the pH drops to 7.7 in the first two hours and settles at a pH of 6.5 while the pH in the acidic solution stays constant at 4.
These results are confirmed in Table 3 showing that the k_f values are the same for all three curves (A',B,C). This result further indicates that the mechanism in operation is film diffusion in view of the fact that gold is converted to the metallic state relatively fast, so that the diffusion inside the carbon never really takes place.

Initial gold concentration

Adsorption tests were performed at three different initial gold concentrations, namely 10, 20 and 30 ppm. Figure 6 and Table 3 (A,D,E,F) shows that there is a change in the adsorption curve for the three different initial gold concentrations. The A value increases with the increase of the initial gold-iodide concentration in solution. A possible explanation for this is that the gold-iodide reduces onto the surface of the carbon, and over time this 'metallic gold layer' blinds of the surface , so that it becomes increasingly more difficult for the complex ion to find a suitable spot on the carbon surface. From the results in Figure 6 it seems that at higher initial gold-iodide concentrations the adsorption mechanism tends to become inter-particle diffusion. This is confirmed by previous results of Hiskey and Qi (7) who found minute amounts of metallic gold inside the carbon matrix.

Iodine/iodide concentration

The solubility of iodine depends on the aqueous concentration of iodine. On dissolution the iodide forms poly-iodide complexes of which the tri-iodide ion dominates (Equation 4). The tri-iodide ion is the main oxidizing agent in the solution.

$$I_2\ (aq) + I^-\ (aq) = I_3^-\ (aq) \tag{4}$$

Figure 7 shows the adsorption profiles when the concentration of the I_2, I^- and I_3^- ions were changed. When only iodine crystals were added to the solution, the iodine still partially dissolved as there was still an excess of iodide in the solution. In the case where both iodine and iodide were added to the solution, nearly all the iodine dissolved. This means that the concentration of tri-iodide ions was higher in both of the previous cases then in the stock solution. However when $Na_2S_2O_3$ was added to the solution all the iodine was oxidized to iodide, so that no tri-iodide could be formed. As seen in Figure 7, both the adsorption kinetics and equilibrium changed. The following possible explanations were offered to describe why the kinetics and equilibrium for both the curves [Table 3;(G,H,I)] changed during adsorption :

a) The higher concentration of tri-iodide ions dissolved the reduced gold on the carbon surface. As iodine also adsorbed onto the carbon and partially evaporated into the air, the tri-iodide concentration dropped over time and hence the re-dissolution effect diminished.

b) Competitive adsorption between the gold and iodine takes place on the carbon surface. Baba *et al* (10) found that iodine adsorbs onto activated carbon but they stated that the higher the iodide concentration, the lower the adsorption of iodine onto the carbon.

c) The excessive amount of tri-iodide, oxidises and destroys the carbon surface so that adsorption and reduction of the gold-iodide is inhibited. Figure-8 illustrates clearly cracks on the carbon surface when exposed to a solution containing I^-/I_2 and gold-iodide.

Carbon was pretreated for 72 hr with a iodide/iodine solution. In one adsorption experiment, the carbon was further treated with $Na_2S_2O_3$ so that no iodine would be present on the carbon surface. A standard solution of gold-iodide was used for both experiments. Figure 9 shows that the kinetics and equilibrium [Table 3;(J,K)] of the experiment where iodine was still present on the carbon surface is different from when the carbon surface was free of iodine. This sustains the previous assumptions made that I_3^- is re-dissolving the elemental gold reduced on the carbon surface and competitive adsorption with iodine takes place.

Dissolved oxygen

Adsorption experiments were performed at different concentrations of dissolved oxygen. This was obtained by bubbling pure oxygen or nitrogen through the reactor from thirty minutes before and during the experiment. While bubbling the nitrogen through the solution the concentration of dissolved oxygen dropped from 7.8 ppm to 0.1 ppm, while with the oxygen bubbling through, the concentration rose to 31.5 ppm. From Figure 10 and Table 3 (L,M) it can be seen that the concentration of dissolved oxygen has no effect on the adsorption of the gold-iodide onto activated carbon. As stated by Adams (11), oxygen oxidises mainly the functional groups on carbon. As most functional groups are situated in the micro-pores, the oxidation or non-oxidation of the groups will not influence the adsorption, as hardly any intra-particle diffusion takes place.

CONCLUSIONS

In this paper factors influencing the adsorption of gold from iodide solutions onto activated carbon was discussed. Film diffusion mechanism is shown to be the dominant mechanism for the adsorption of the gold-iodide. The fact that the gold-iodide reduces mainly to metallic gold on the carbon surface establishes a high difference in gold-iodide concentration over the film boundary and so creates a strong driving force for mass transfer. From the mixing experiments, it was clearly seen that the film diffusion coefficient (k_f) changes linearly with an increase in impeller speed. Both mixing and the interruption experiments indicate clearly that film diffusion is the predominant rate transfer mechanism.

The equilibrium studies demonstrate that the equilibrium loading for gold-iodide is higher then for gold cyanide. The pH level of the solution did not change the adsorption characteristics significantly. Initial gold-iodide, iodine and tri-iodide concentrations influenced both the kinetics and equilibrium of adsorption. Scanning electron micrographs taken of the carbon's surface showed the presence of elemental gold.

ACKNOWLEDGEMENT

MINTEK assisted this project financially.

NOMENCLATURE

A	parameter in Freundlich isotherm
A_c	effective external surface of carbon [m^2]
C_c^o	initial gold loading on carbon surface [$mg.g^{-1}$]
C_s^e	equilibrium solution concentration [$mg.l^{-1}$]
C_s^o	initial solution concentration [$mg.l^{-1}$]
C_s	solution concentration [$mg.l^{-1}$]
d_p	average carbon particle diameter [m]
k_f	external film transfer coefficient [$m.s^{-1}$]
m_c	mass of carbon [kg]
m_s	mass of solution [kg]
n	empirical constant in Freundlich isotherm
C_c^e	gold loading on carbon [$mg.g^{-1}$ carbon]
V_s	volume of solution [m^3]

Greek letters

ρ	apparent density of carbon [$kg.m^{-3}$]

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FIGURE CAPTIONS

Figure 1	Film transfer coefficient as a function of stirring speed for gold cyanide and gold-iodide in a batch reactor.
Figure 2	Effect of interruption on adsorption profile of gold-iodide onto activated carbon. (C_c^o = 20 ppm; m_c = 0.5 g; N = 300 rpm; pH = 6.5; V_s = 1 L)
Figure 3	Equilibrium isotherms for gold cyanide and gold-iodide.
Figure 4	Scanning Electron Micrograph showing elemental gold crystals on the surface of activated carbon.
Figure 5	Adsorption profile of gold-iodide onto activated carbon at different pH's. (C_c^o = 20 ppm; m_c = 1 g; N = 300 rpm; V_s = 1 L)
Figure 6	Adsorption profile of gold-iodide onto activated carbon at different initial gold-iodide concentrations. (m_c = 0.2 g; N = 300 rpm; pH = 6.5; V_s = 1 L)
Figure 7	Adsorption profile of gold-iodide onto activated carbon at different concentrations of iodine, iodide and tri-iodide. (C_c^o = 20 ppm; m_c = 0.5 g; N = 300 rpm; pH = 6.5; V_s = 1 L)
Figure 8	Scanning Electron Micrograph of activated carbon surface when exposed to a standard gold-iodide solution.
Figure 9	Adsorption profile of gold-iodide onto activated carbon showing the influence of pretreatment of carbon with iodine/iodide solution. (C_c^o = 20 ppm; m_c = 0.2 g; N = 300 rpm; pH = 6.5; V_s = 1 L)

Figure 10 Adsorption profile of gold-iodide onto activated carbon at different levels of dissolved oxygen.

($C_s^\circ = 20$ ppm; $m_c = 0.2$ g; $N = 300$ rpm; pH = 6.5; $V_s = 1$ L)

Table 1 : FILM TRANSFER COEFFICIENTS AT DIFFERENT STIRRING SPEEDS

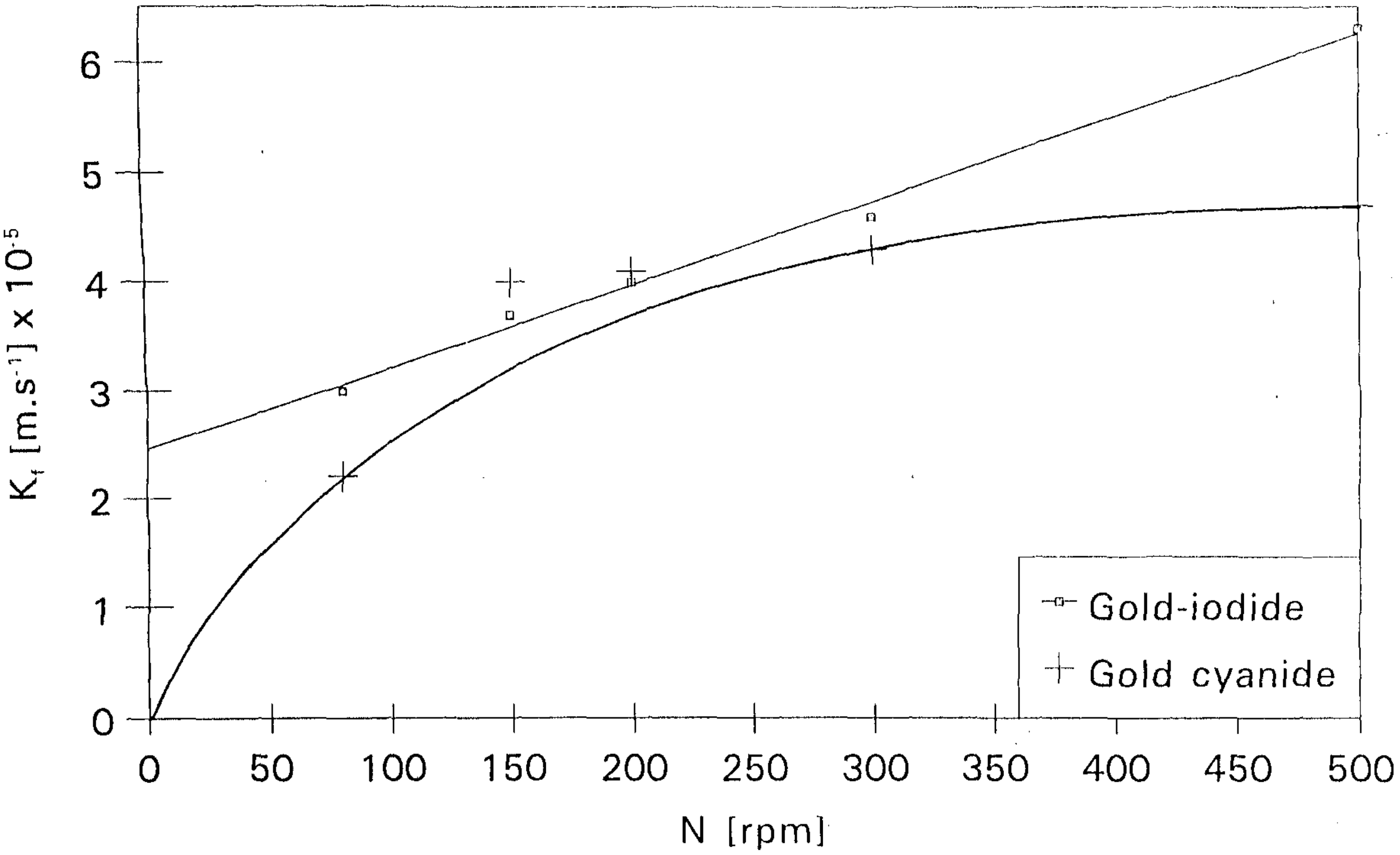
Stirring rate [rpm]	Gold-iodide k_f [m.s^{-1}] x 10^5	Gold cyanide k_f [m.s^{-1}] x 10^5
80	3.0	2.2
150	3.7	4.0
200	4.0	4.1
300	4.6	4.3
500	6.3	4.7

Table 2 : COMPARISON BETWEEN EQUILIBRIUM KINETIC CONSTANTS FOR GOLD-IODIDE AND GOLD CYANIDE

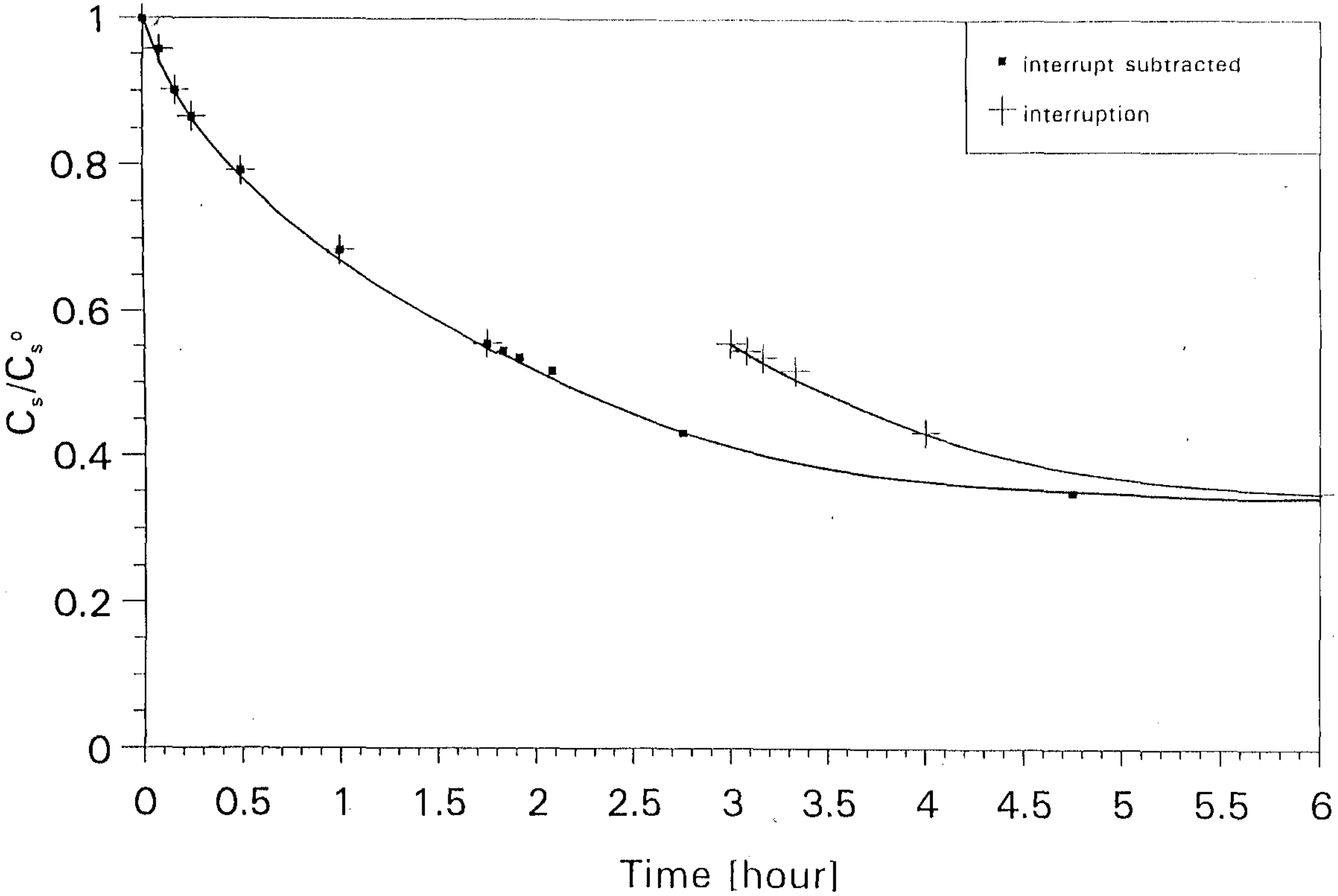
	A constant	**n constant**
gold-iodide	76.11	0.25
gold cyanide	13.73	0.16

TABLE 3 : SENSITIVITY OF MASS TRANSFER PARAMETERS

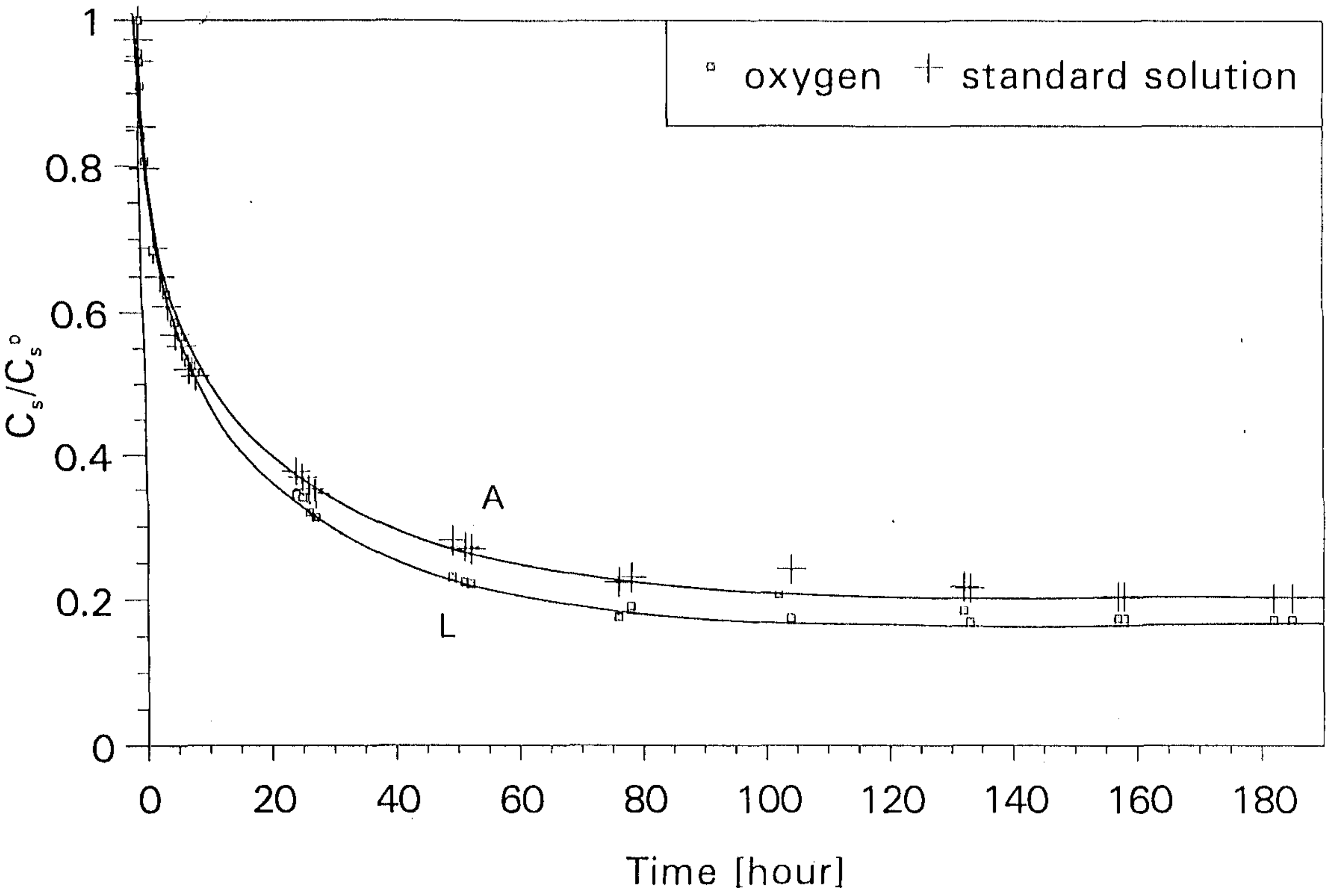
Curve	Conditions	K_f [m.s^{-1}] x 10^5	A	n
A	"standard" pH = 6.5 [Au] = 20 ppm	4.0	55	0.25
A'	pH = 6.5	4.6	80	0.25
B	pH = 4	4.6	80	0.25
C	pH = 10	4.6	80	0.25
D	[Au] = 10 ppm	4.6	60	0.25
E	[Au] = 30 ppm	4.6	58	0.33
F	[Au] = 50 ppm	4.6	95	0.25
G	only I^-	3.0	60	0.25
H	0.01 M I_2 added	3.0	9	0.25
I	0.02 M I_2 added	3.0	5.5	0.25
J	pretreated with I^-/I_2 and $Na_2S_2O_3$	1.7	70	0.25
K	pretreated with I^-/I_2	0.8	53	0.05
L	[dissolved O_2] = 31.5 ppm	4.6	57	0.05



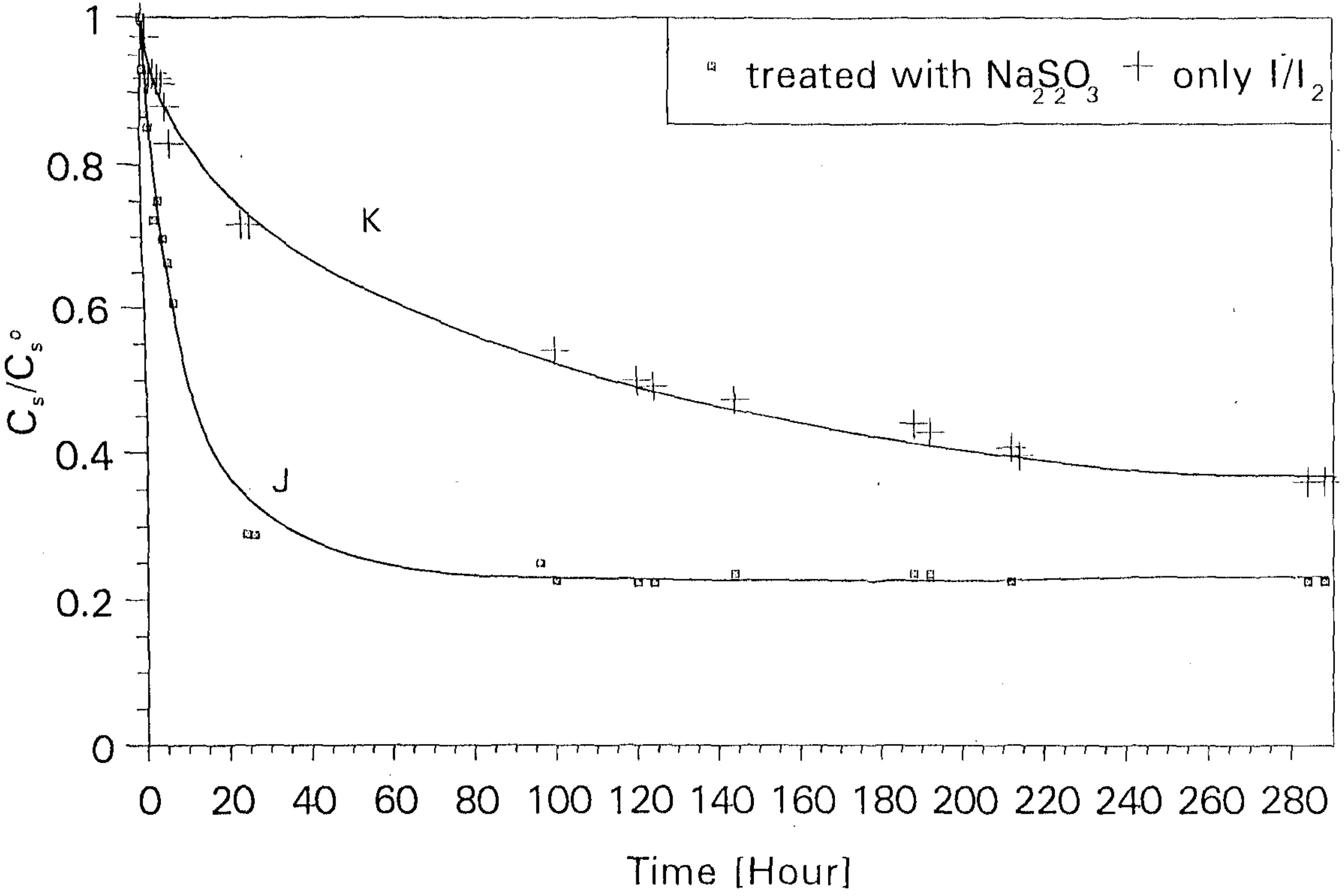
[Figure 1 : Teirlinck and Petersen]



[Figure 2 : Teirlinck and Petersen]



[Figure 10 : Teirlinck and Petersen]


treated with $Na_2S_2O_3$
only I^-/I_2
K
J
C_s/C_s^o
Time [Hour]
1
0.8
0.6
0.4
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0
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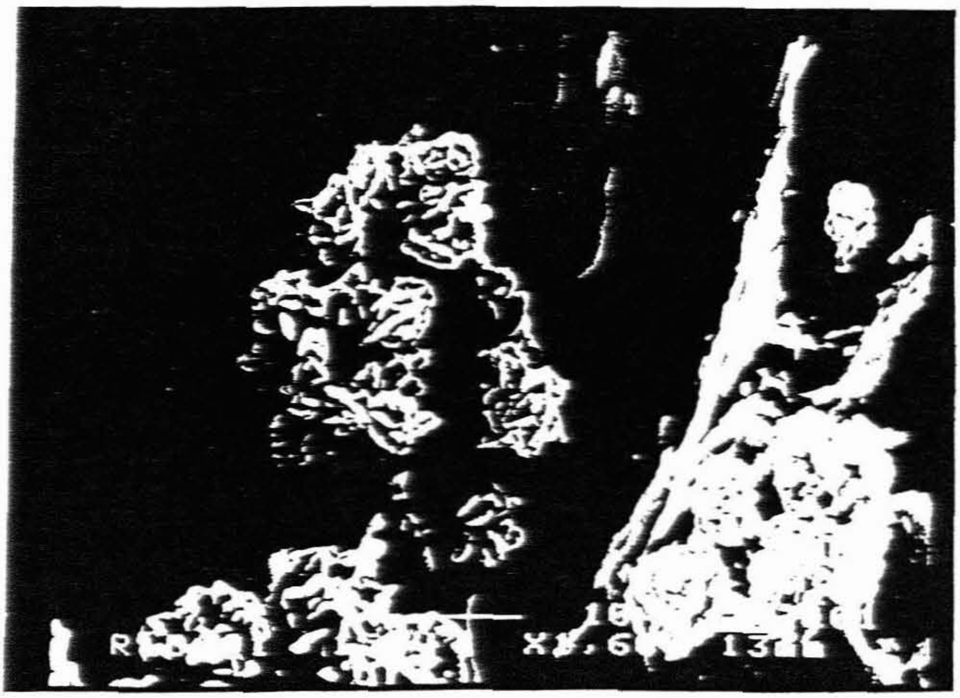

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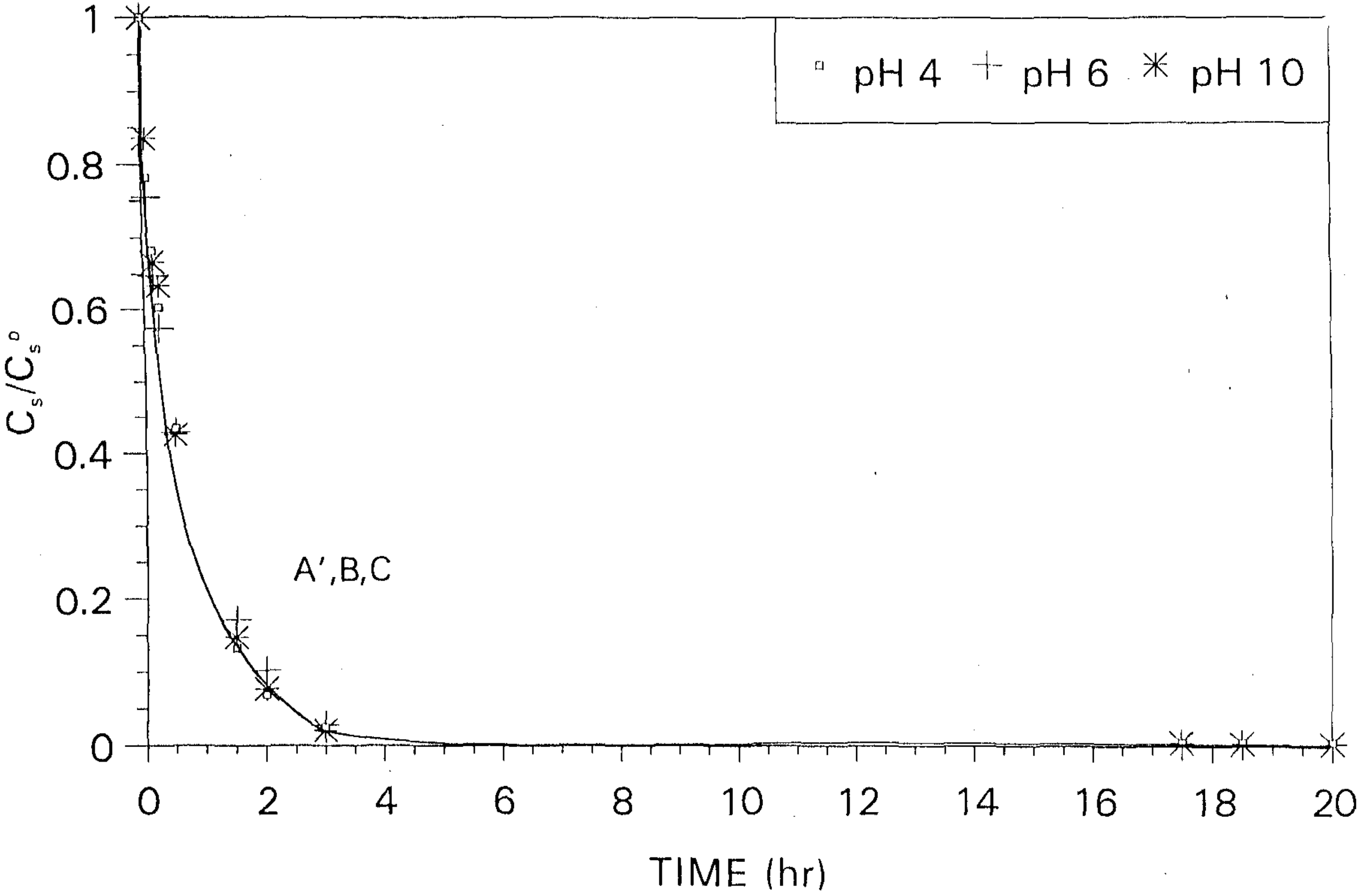
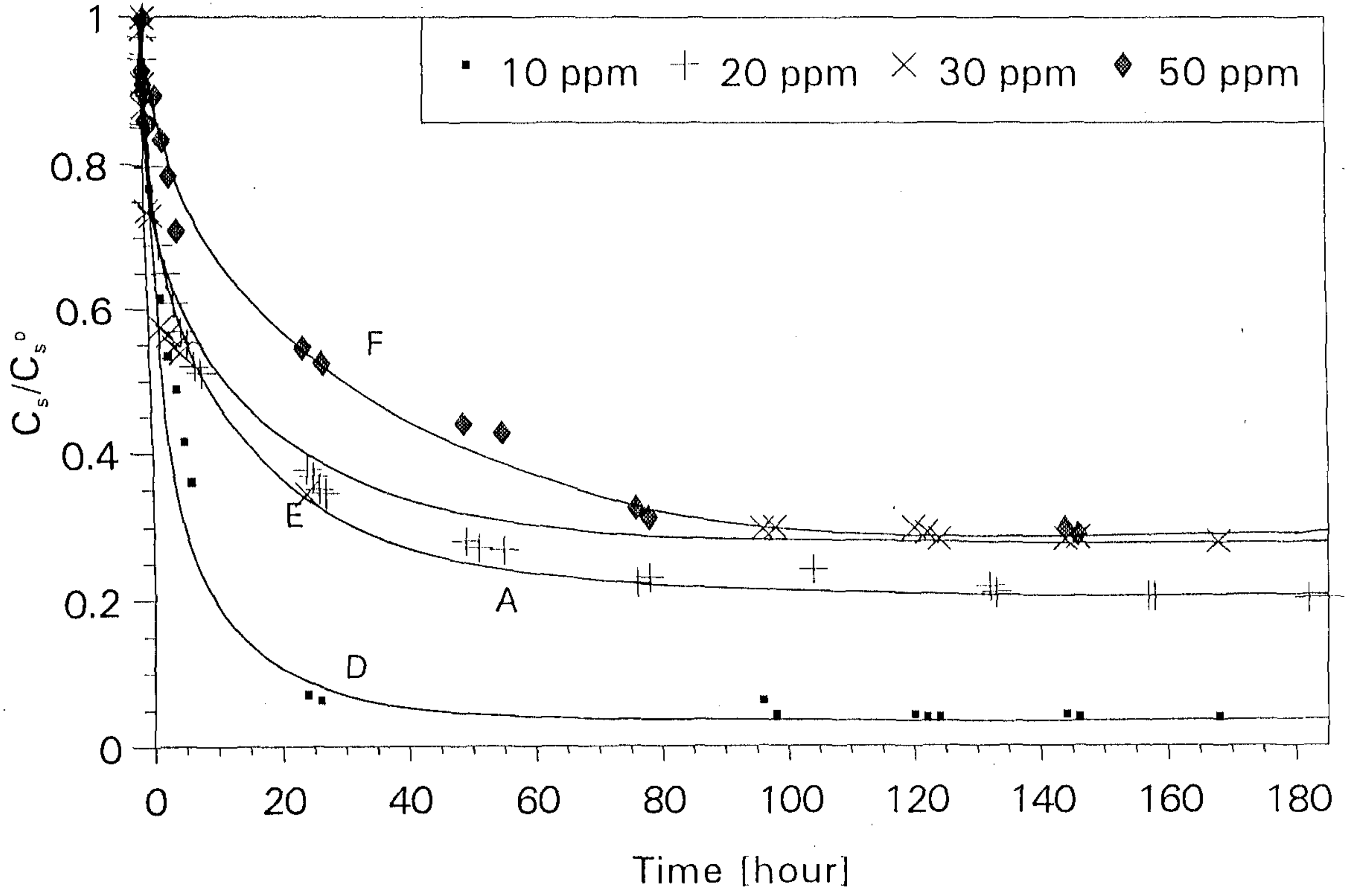
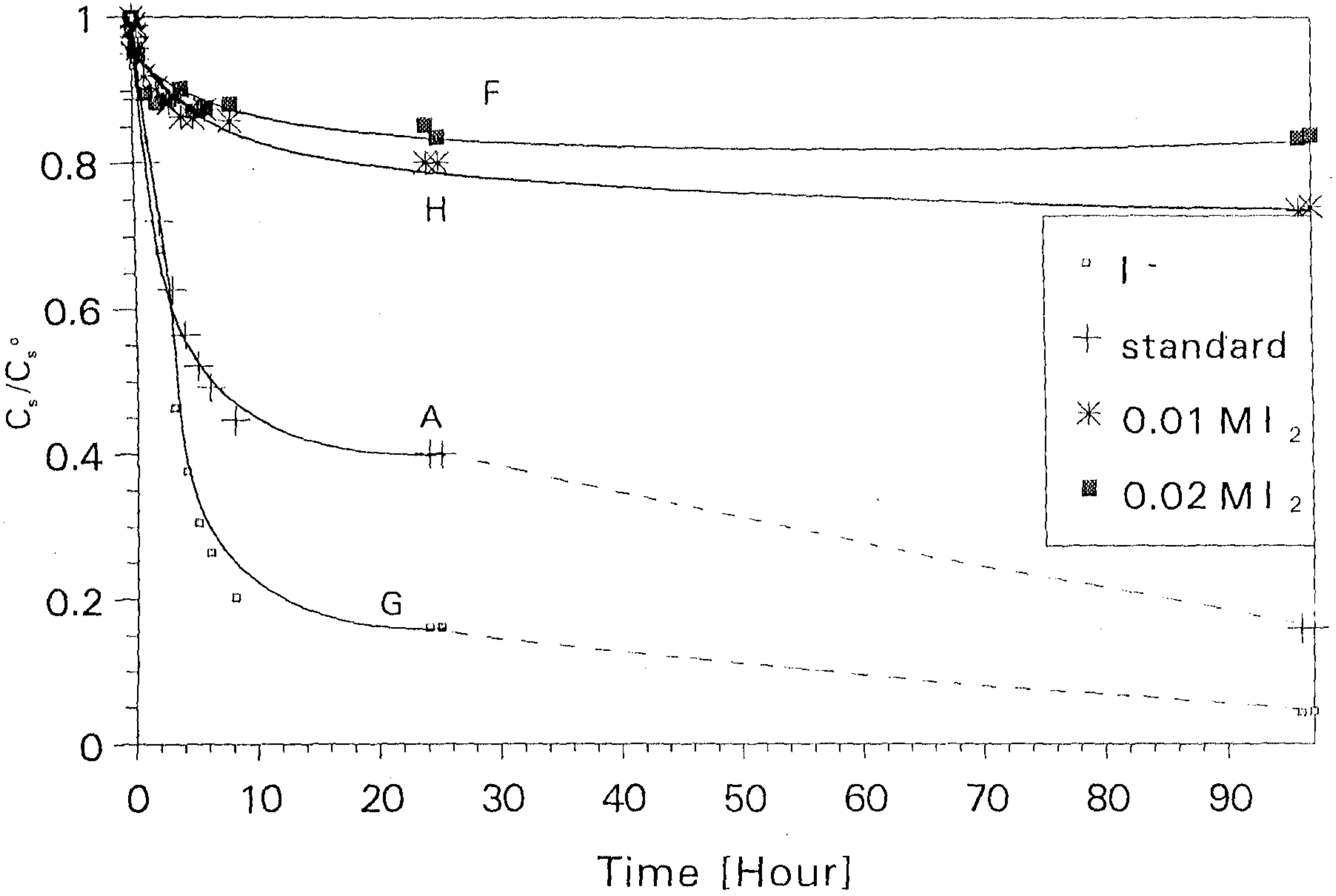


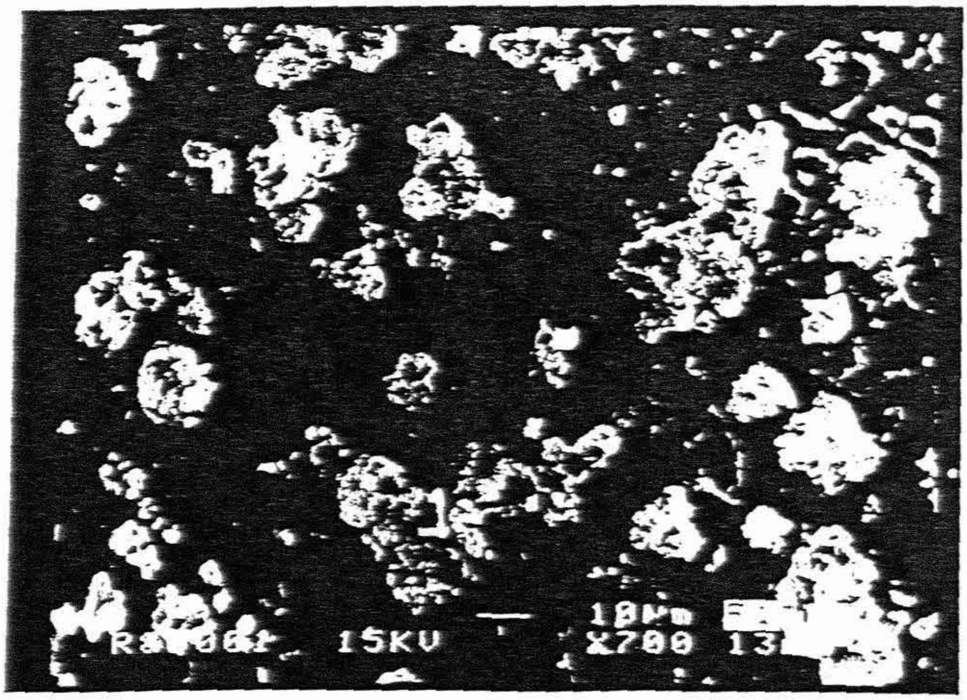
[Figure 5 : Teirlinck and Petersen]



[Figure 6 : Teirlinck and Petersen]



[Figure 7 : Teirlinck and Petersen]



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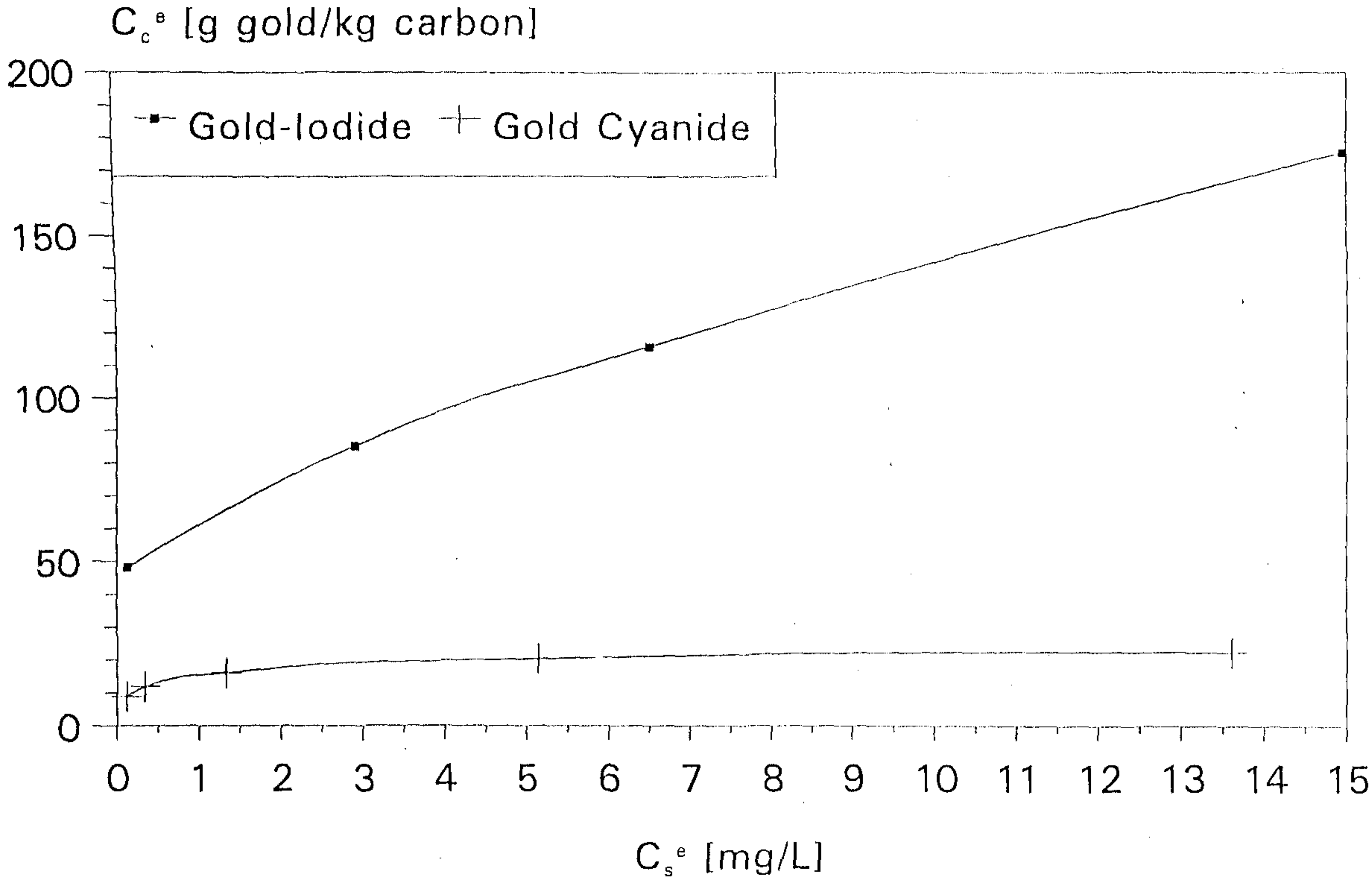

(Figure 3 : Teirlinck and Petersen)

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Factors Influencing the Adsorption of Gold-Iodide onto Activated Carbon

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ABSTRACT

Activated carbon has found increasing application during the past decade as an adsorbent for gold from cyanide leached pulps. As result of practical and theoretical advancements in recent years, the carbon-in-pulp (CIP) process has become the preferred method for gold extraction from cyanided slurries. Lately, environmental considerations have led to the investigation of alternative leaching processes. One group of lixiviants studied is the halogens, such as bromine, chlorine, and iodine. It is the aim of this paper to investigate the factors influencing the adsorption of gold from iodide solutions onto a coconut-shell-type activated carbon. Equilibrium loadings on the carbon indicated clearly that gold-iodide has a higher loading profile than has gold cyanide. The Freundlich isotherm fitted the equilibrium curve for gold-iodide adsorption on carbon. The experimental results indicated that the pH level, iodide, and dissolved oxygen concentration had little or no influence on the kinetic and equilibrium parameters in a film diffusion model. However, the initial gold, iodine, and tri-iodide concentrations altered both the rate and equilibrium of gold-iodide adsorption significantly. Scanning electron microscopy showed that elemental gold deposited on the carbon surface influences the high film transfer coefficients obtained for gold-iodide adsorption.

INTRODUCTION

Main concerns in the mining industry at present are the increases in environmental awareness and of environmental legislation. Thus, alternative methods become more and more important whereby the existing processes can be converted to satisfy these potential requirements. The preferred method of gold extraction at this moment is the carbon-in-pulp

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(CIP) process. This involves the extraction of the gold from cyanide leached pulps by means of activated carbon. Although potassium cyanide is the most economical lixiviant at the moment, it raises certain concerns. These include the formation of deadly hydrogen cyanide gas, adsorption through the skin, and accidental ingestion of cyanide salts. Dangerous situations can be created when cyanide forms organic and inorganic complexes which are difficult to destroy by conventional methods and which can contaminate effluent streams. Thus, a need is created for the investigation of alternative lixiviants for gold dissolution.

Thiourea, chloride, bromide, and iodide are alternative lixiviants that have been investigated recently. Previous studies (1–5) indicate that gold leaches easily in a relative dilute iodine/iodide solution. Of all the halides, iodide forms the most stable auro-complex and is stable over the widest pH range; up to pH 14 (3, 5).

Hiskey and Jiang (6) investigated the loading of gold onto carbon in chloride solutions and found that Au(III) is reduced to metallic gold on the carbon surface and the rate of reduction is controlled by boundary layer diffusion. Furthermore, these authors found that an acid environment had no effect on gold reduction. Hughes and Linge (7) concluded that the rate-controlling step was mass transfer over the film boundary. Sun and Yen (8) observed that the concentration of chloride and hydrogen ions (acidity) did not play a role in the adsorption rate. However, dissolved chlorine decreased the rate of gold adsorption, probably due to the redissolution of gold from the carbon surface by the aqueous chlorine.

The adsorption of gold bromide by activated carbon was studied by Pesic and Storhok (9). They showed that gold(III) bromide is mainly adsorbed in the ionic form but also follows a first-order rate reaction and was affected mainly by the concentration of free bromide due to competitive adsorption.

Hiskey and Qi (10) investigated the nature of gold uptake from iodide solutions onto activated carbon and suggested a combined process of adsorption and reduction. Although these authors speculated that gold is reduced on the outer surface of the carbon and that some gold is adsorbed in the porous structure of the carbon, little information on the mechanism or parameters affecting the nature of gold-iodide adsorption was provided. It is the objective of this paper to investigate the factors influencing the adsorption of gold from iodide solutions.

THEORY

Equilibrium Constants

The Freundlich isotherm (Eq. 1) fitted the equilibrium curves for the adsorption of gold-iodide onto activated carbon. The values for A and n

were obtained by drawing a graph of ln C_c^e against ln C_s^e. A straight line is produced of slope n and intercept ln A. The parameters A and n are compared in Table 2 to values obtained from gold cyanide equilibrium data.

$$C_c^e = A(C_s^e)^n \tag{1}$$

Mass Transfer Coefficient

Johns (11) derived a model for the adsorption of gold cyanide onto activated carbon. This model expressed an equation (Eq. 2) which derives the gold concentration in solution at any given time in a batch reactor. The following assumptions were made in developing the model:

- Interdiffusion is treated as quasi-stationary.
- Diffusion across the film is fast compared to the concentration changes at the film boundary.
- The film is treated as a planar layer (one-dimensional diffusion).
- The particles can be treated as equivalent spheres with a homogeneous outer surface.

A computer program was written to obtain the k_f values (Table 3) for the adsorption curves.

$$\frac{dC_s}{dt} = -k_f\left(\frac{A_c}{V_s}\right)C_s + k_f\left(\frac{A_c}{V_s}\right)A\left[C_c^0 + \left(\frac{m_s}{m_c}\right)C_s^0 + \left(\frac{m_s}{m_c}\right)C_s\right]^n \tag{2}$$

EXPERIMENTAL

All experiments were performed in a 1-L baffled batch reactor. Agitation was provided by a flat blade impeller, driven by a Heidolph variable speed motor. The impeller speed was kept constant at 300 rpm except for experiments performed for the determination of the film transfer coefficient. Fine gold nuggets (1 g) were dissolved in a 1-L volumetric flask using 0.1 M KI and 5×10^{-3} M I_2 to obtain a 1000 ppm Au solution. All reagents used were of analytical grade and distilled water was used throughout. The pH was adjusted using either a 1 M HCl or 1 M KOH solution and was measured with a Beckmann Φ71 pH meter. The nitrogen and oxygen gases were supplied by Fedgas, and the dissolved oxygen levels were measured with a Hanna HI 8043 dissolved oxygen meter. All experiments were performed at room temperature.

Samples were taken at regular intervals, and the gold concentration was measured using a Varian AA-1275 atomic adsorption spectrophotometer.

The concentrations of I_2 and I^- were obtained by titration against NaS_2O_3 and KIO_3 respectively. A coconut shell activated carbon (average diameter of 1.4 mm) provided by ACIX was used as an adsorbent. Initially, 1 g of carbon was used, but due to the rapid drop in gold-iodide concentration to almost 0 ppm in the reactor, it was decided to decrease the mass of carbon to 0.2 g. Equilibrium tests were performed over a period of 3 weeks.

RESULTS AND DISCUSSION

Adsorption experiments with gold-iodide were used to evaluate kinetic and equilibrium parameters in the film diffusion model. These parameters will be discussed qualitatively for each of the factors influencing gold-iodide adsorption.

Mixing

The stirring speed influences the rate of mass transfer of gold-iodide from the solution to the carbon surface. The reason behind this is that the increase in stirring speed decreases the diffusion layer thickness surrounding the carbon particle. This decrease in thickness will decrease the film diffusion coefficient (k_f) in a film diffusion model.

Initially, the purpose was to define the driving mechanism behind the adsorption of the gold-iodide complex. From a preliminary test it was seen that the gold concentration dropped relatively fast versus the same experiment using gold cyanide. This was a first indication that film diffusion might play a pivotal role in the adsorption mechanism. Adsorption tests were performed at five different stirring speeds with samples taken at regular intervals for the first 30 minutes with an initial gold concentration of 20 ppm for all the experiments. As explained by Van Deventer (12), a plot of *ln* (C_s^0/C_s) *versus time yields a straight line that passes* through the origin, and the k_f value can be determined from the slope of this line:

$$\ln\left(\frac{C_s^0}{C_s}\right) = \frac{6k_f m_c}{\rho d_p V_s}\,t, \qquad \text{as } t \to 0 \tag{3}$$

Figure 1 shows a plot of the coefficients (Table I) obtained for both gold-iodide and gold cyanide against the impeller speed. While the curve for gold cyanide plateaus off due to intraparticle diffusion taking over from film diffusion, the curve for the gold-iodide yields a straight line,

TABLE I
Film Transfer Coefficients at Different Stirring Speeds

Stirring rate (rpm)	Gold-iodide k_f ($m \cdot s^{-1} \times 10^5$)	Gold cyanide k_f ($m \cdot s^{-1} \times 10^5$)
80	3.0	2.2
150	3.7	4.0
200	4.0	4.1
300	4.6	4.3
500	6.3	4.7

indicating that film diffusion remains the primary mechanism of mass transfer.

An interruption test is a useful method for differentiating between intraparticle diffusion and film diffusion. The carbon was separated from the solution for 1.5 hours. If any intraparticle diffusion has taken place, this separation time would allow mass transfer to continue in the carbon pores. The gold-iodide would diffuse further into the pores, thus creating a higher driving force for mass transfer immediately after reimmersion of the carbon in the solution. As seen from Fig. 2, it is clear that no increase in kinetics takes place after the readdition of the carbon to the solution. This means that film diffusion is the prominent mechanism in operation.

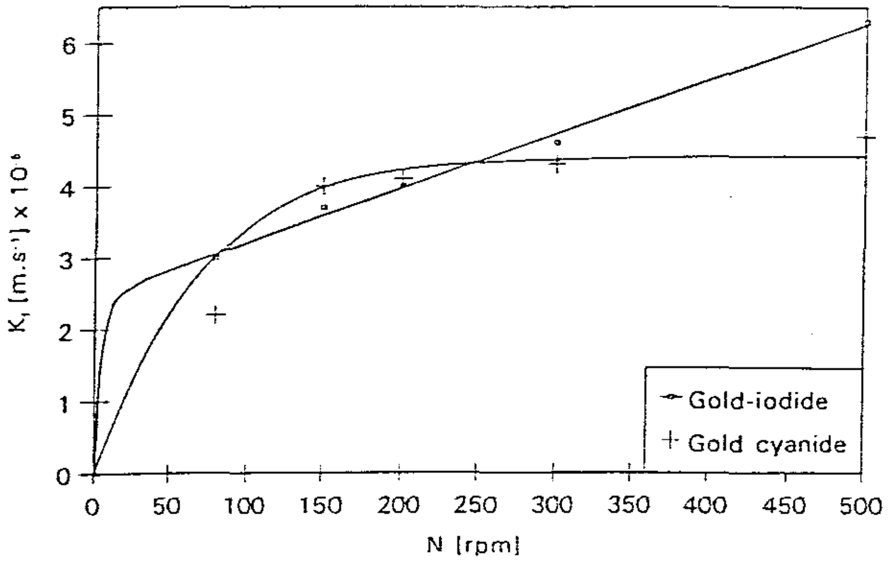

FIG. 1 Film transfer coefficient (k_f) as a function of stirring speed for gold cyanide and gold-iodide in a batch reactor.

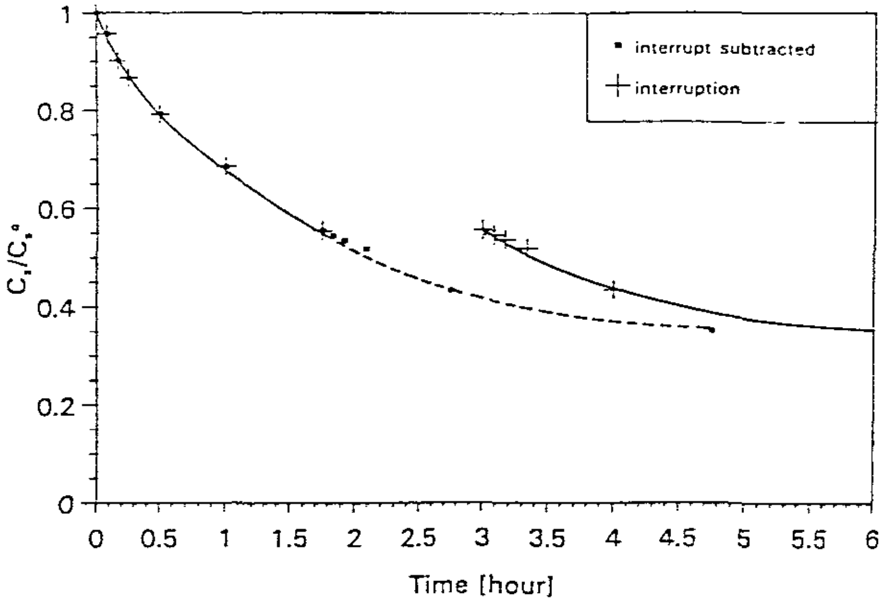

FIG. 2 Effect of interruption on adsorption profile of gold-iodide onto activated carbon (C_c^0 = 20 ppm; m_c = 0.5 g; N = 300 rpm; pH 6.5; V_s = 1 L).

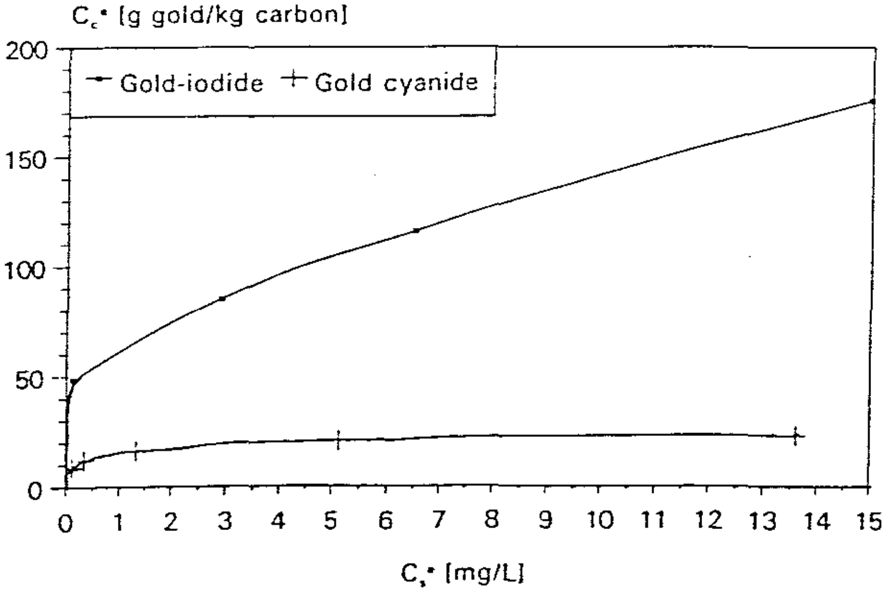

FIG. 3 Equilibrium isotherms for gold cyanide and gold-iodide.

Equilibrium Studies

Equilibrium experiments were performed with different initial concentrations for both gold cyanide and gold-iodide. As seen from Fig. 3 and Table 2, the equilibrium loading on the carbon for the gold-iodide is higher than the equilibrium loading for the gold cyanide. This can be explained through the fact that the gold-iodide complex is reduced to metallic gold and (see Fig. 4) accumulates on the carbon surface, whereas in the case of gold cyanide, diffusion into the carbon particle can take place.

pH

Adsorption tests were performed at three different pHs: 4, 6, and 10. The potential–pH equilibrium diagram for the gold-iodide system illus-

TABLE 2
Comparison between Equilibrium Kinetic Constants for Gold-Iodide and Gold Cyanide

	A constant	*n* constant
Gold-iodide	76.11	0.25
Gold cyanide	13.73	0.16

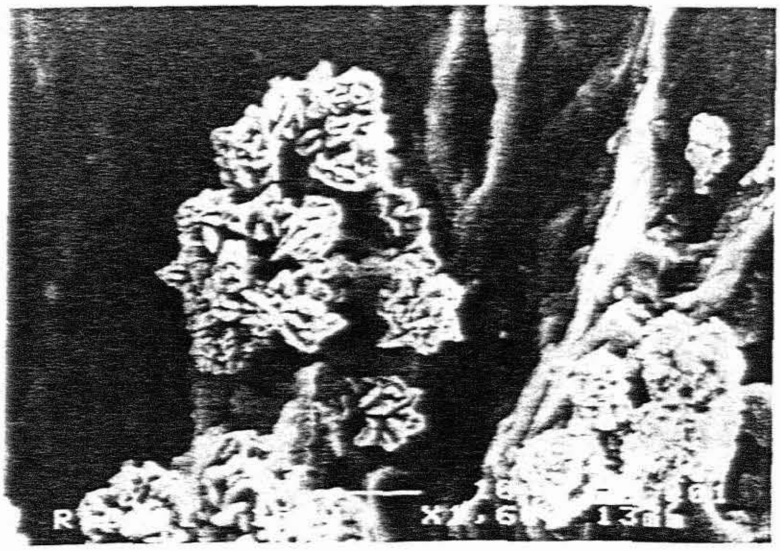

FIG. 4 Scanning electron micrograph showing elemental gold crystals on the surface of activated carbon.

trates that the AuI_2^- complex is soluble up to a pH of 14 (3, 5). Figure 5 shows clearly that pH does not play a role in the adsorption rate, nor does it change the equilibrium loading of gold-iodide for the conditions set out in the figure legend.

These results are confirmed in Table 3 which shows that the k_f values are the same for all three curves (A′, B, C). This result further indicates that the mechanism in operation is film diffusion in view of the fact that gold is converted to the metallic state relatively fast, so diffusion inside the carbon can never really take place.

Initial Gold Concentration

Adsorption tests were performed at four different initial gold concentrations: 10, 20, 30, and 50 ppm. Figure 6 and Table 3 (A, D, E, F) shows that there is a change in the adsorption curve for the four different initial gold concentrations. The A value increases with an increase of the initial gold-iodide concentration in solution. A possible explanation for this is that the gold-iodide reduces onto the surface of the carbon, and over time this "metallic gold layer" blinds the surface, so that it becomes increasingly more difficult for the complex ion to find a suitable spot on the carbon surface. From the results in Fig. 6 it seems that at higher initial

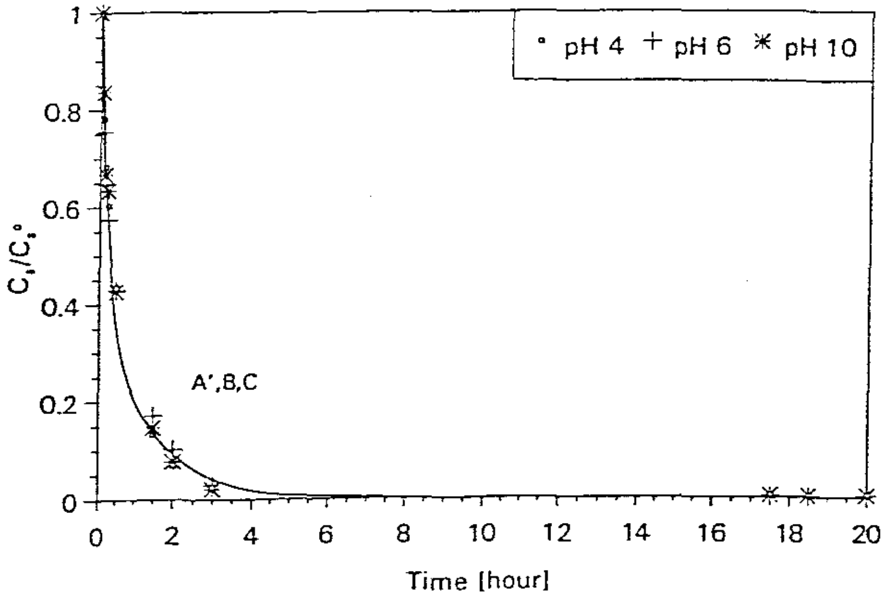

FIG. 5 Adsorption profile of gold-iodide onto activated carbon at different pHs (C_s^0 = 20 ppm; m_c = 1 g; N = 300 rpm; V_s = 1 L).

TABLE 3
Sensitivity of Mass Transfer Parameters

Curve	Conditions	K_f ($m \cdot s^{-1} \times 10^5$)	A	n
A	"standard," pH 6.5, [Au] = 20 ppm	4.0	55	0.25
A′	pH 6	4.6	80	0.25
B	pH 4	4.6	80	0.25
C	pH 10	4.6	80	0.25
D	[Au] = 10 ppm	4.6	60	0.25
E	[Au] = 30 ppm	4.6	68	0.33
F	[Au] = 50 ppm	4.6	95	0.25
G	Only I^-	3.0	60	0.25
H	0.01 M I_2 added	3.0	9	0.25
I	0.02 M I_2 added	3.0	5.5	0.25
J	Pretreated with I^-/I_2 and $Na_2S_2O_3$	1.7	70	0.25
K	Pretreated with I^-/I_2	0.8	53	0.05
L	[Dissolved O_2] = 31.5 ppm	4.6	57	0.05

gold-iodide concentrations the adsorption mechanism tends to become interparticle diffusion. This is confirmed by previous results of Hiskey and Qi (10) who found minute amounts of metallic gold inside the carbon matrix.

Iodine/Iodide Concentration

The solubility of iodine depends on the aqueous concentration of iodine. On dissolution the iodide forms poly-iodide complexes of which the tri-iodide ion dominates (Eq. 4). The tri-iodide ion is the main oxidizing agent in the solution.

$$I_2(aq) + I^-(aq) = I_3^-(aq) \tag{4}$$

Figure 7 shows the adsorption profiles when the concentrations of the I_2, I^-, and I_3^- ions were changed. When only iodine crystals were added to the solution, the iodine still partially dissolved as there was still an excess of iodide in the solution. In the case where both iodine and iodide were added to the solution, nearly all the iodine dissolved. This means that the concentration of tri-iodide ions was higher in both of the previous cases than in the stock solution. However, when NaS_2O_3 was added to the solution, all the iodine was oxidized to iodide, so that no tri-iodide could be formed. As seen in Fig. 7, both the adsorption kinetics and equilibrium changed. The following possible explanations were offered to de-

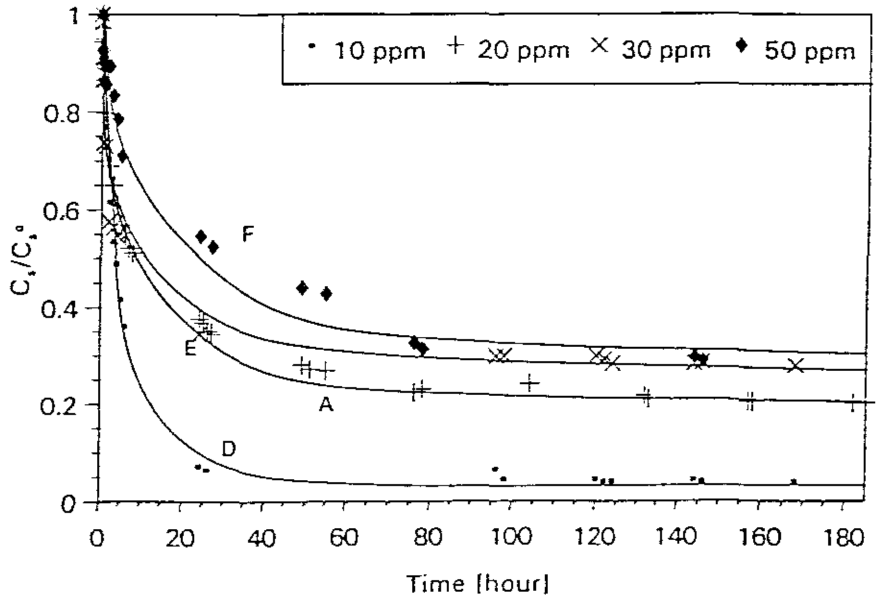

FIG. 6 Adsorption profile of gold-iodide onto activated carbon at different initial gold-iodide concentrations (m_c = 0.2 g; N = 300 rpm; pH 6.5; V_s = 1 L).

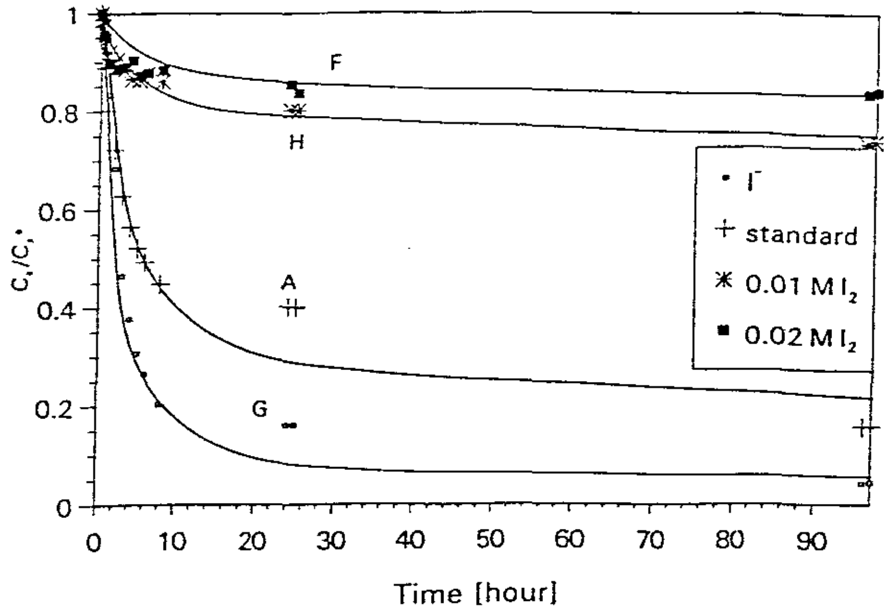

FIG. 7 Adsorption profile of gold-iodide onto activated carbon at different concentrations of iodine, iodide, and tri-iodide (C_c^0 = 20 ppm; m_c = 0.5 g; N = 300 rpm; pH 6.5; V_s = 1 L).

scribe why the kinetics and equilibrium for the curves [Table 3 (A, G, H, I)] changed during adsorption.

1. The higher concentration of tri-iodide ions dissolved the reduced gold on the carbon surface. As iodine also adsorbed onto the carbon and partially evaporated into the air, the tri-iodide concentration dropped over time and hence the redissolution effect diminished.
2. Competitive adsorption between the gold and iodine takes place on the carbon surface. Baba et al. (13) found that iodine adsorbs onto activated carbon, but they stated that the higher the iodide concentration, the lower the adsorption of iodine onto the carbon.
3. The excessive amount of tri-iodide oxidizes and destroys the carbon surface so that adsorption and reduction of the gold-iodide is inhibited. Figure 8 clearly illustrates cracks on the carbon surface following exposure to a solution containing I^-/I_2 and gold-iodide.

Carbon was pretreated for 72 hours with a iodide/iodine solution. In one adsorption experiment the carbon was further treated with NaS_2O_3 so that no iodine would be present on the carbon surface. A standard solution of gold-iodide was used for both experiments. Figure 9 shows that the kinetics and equilibrium [Table 3 (J, K)] of the experiment where iodine was still present on the carbon surface are different from when the carbon surface was free of iodine. This sustains the previous assumptions

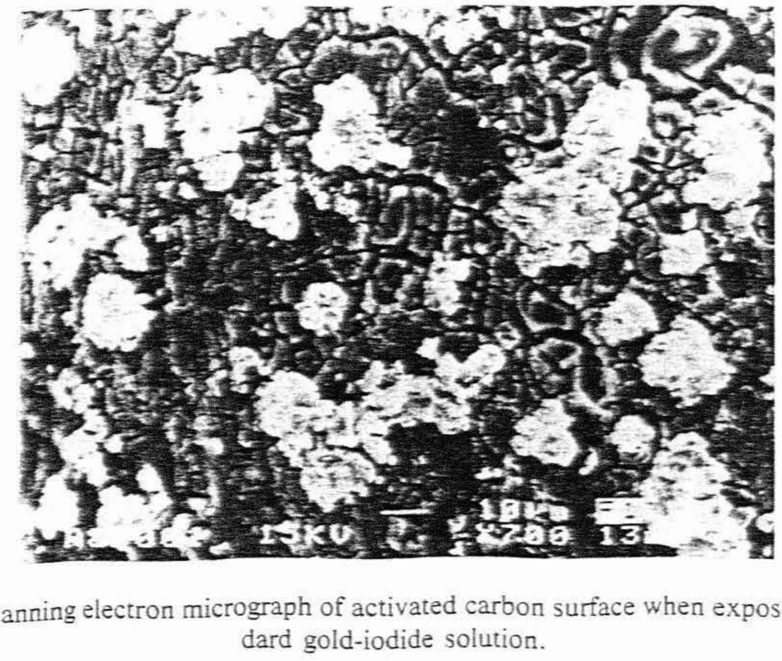

FIG. 8 Scanning electron micrograph of activated carbon surface when exposed to a standard gold-iodide solution.

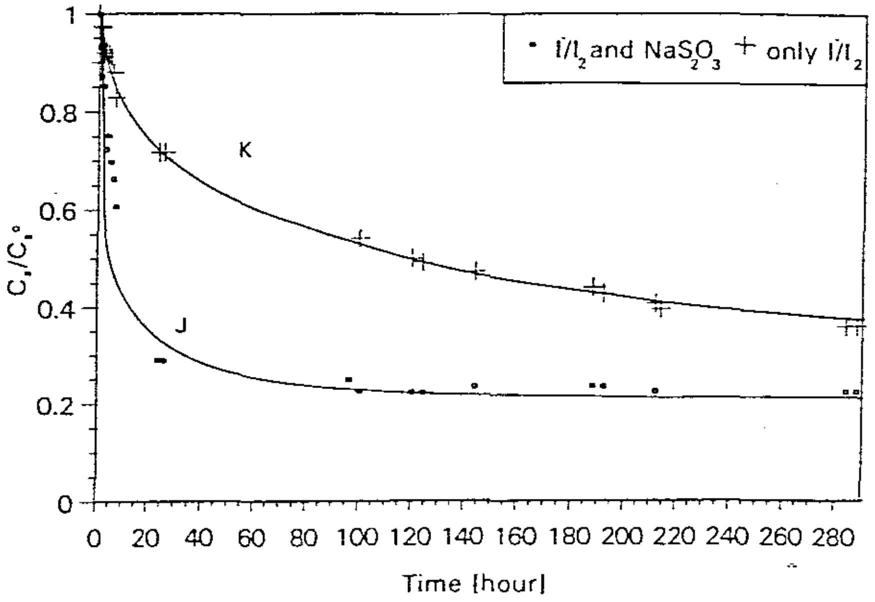

FIG. 9 Adsorption profile of gold-iodide onto activated carbon showing the influence of pretreatment of carbon with iodide/iodide solution (C_s^0 = 20 ppm; m_c = 0.2 g; N = 300 rpm; pH 6.5; V_s = 1 L).

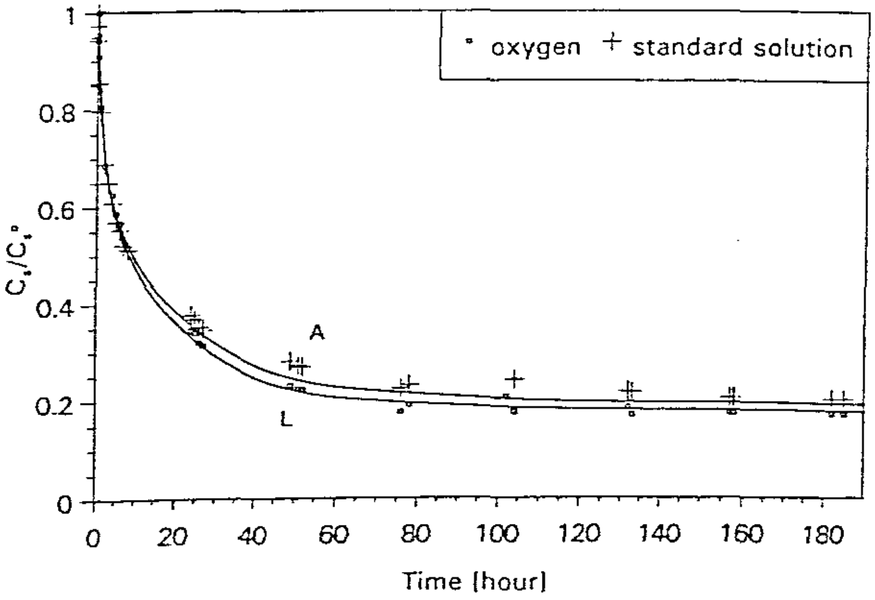

FIG. 10 Adsorption profile of gold-iodide onto activated carbon at different levels of dissolved oxygen (C_s^0 = 20 ppm; m_c = 0.2 g; N = 300 rpm; pH 6.5; V_s = 1 L).

scribe why the kinetics and equilibrium for the curves [Table 3 (A, G, H, I)] changed during adsorption.

1. The higher concentration of tri-iodide ions dissolved the reduced gold on the carbon surface. As iodine also adsorbed onto the carbon and partially evaporated into the air, the tri-iodide concentration dropped over time and hence the redissolution effect diminished.
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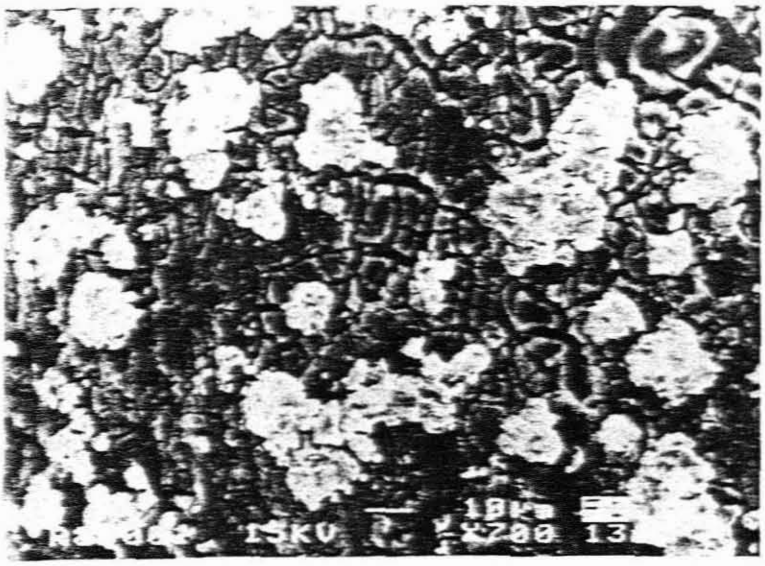

FIG. 8 Scanning electron micrograph of activated carbon surface when exposed to a standard gold-iodide solution.

made that I_3^- redissolves the elemental gold reduced on the carbon surface, and competitive adsorption with iodine takes place.

Dissolved Oxygen

Adsorption experiments were performed at different concentrations of dissolved oxygen. This was obtained by bubbling pure oxygen or nitrogen through the reactor from 30 minutes before and during the experiment. While bubbling the nitrogen through the solution the concentration of dissolved oxygen dropped from 7.8 to 0.1 ppm, while with the oxygen bubbling through the concentration rose to 31.5 ppm. From Fig. 10 and Table 3 (L, M) it can be seen that the concentration of dissolved oxygen has no effect on the adsorption of the gold-iodide onto activated carbon. As stated by Adams (14), oxygen mainly oxidizes the functional groups on carbon. As most functional groups are situated in the micro-pores, the oxidation or nonoxidation of the groups will not influence the adsorption because hardly any intraparticle diffusion takes place.

CONCLUSIONS

In this paper the factors influencing the adsorption of gold from iodide solutions onto activated carbon were discussed. The film diffusion mechanism was shown to be the dominant mechanism for the adsorption of the gold-iodide. The fact that gold-iodide reduces mainly to metallic gold on the carbon surface establishes a large difference in gold-iodide concentration over the film boundary and so creates a strong driving force for mass transfer.

It was clearly seen from mixing experiments that the film diffusion coefficient (k_f) changes linearly with an increase in impeller speed. Both mixing and interruption experiments clearly indicated that film diffusion is the dominant rate transfer mechanism.

Equilibrium studies demonstrated that equilibrium loading for gold-iodide is higher than for gold cyanide. The pH level of the solution did not change the adsorption characteristics significantly. Initial gold-iodide, iodine, and tri-iodide concentrations influenced both the kinetics and equilibrium of adsorption. Scanning electron micrographs taken of the carbon's surface showed the presence of elemental gold.

ACKNOWLEDGMENT

MINTEK assisted this project financially.

NOMENCLATURE

A	parameter in Freundlich isotherm
A_c	effective external surface of carbon (m^2)
C_c^0	initial gold loading on carbon surface ($mg \cdot g^{-1}$)
C_c^e	equilibrium gold loading on carbon surface ($mg \cdot g^{-1}$)
C_s^0	initial solution concentration ($mg \cdot L^{-1}$)
C_s^e	equilibrium solution concentration ($mg \cdot L^{-1}$)
C_s	solution concentration ($mg \cdot L^{-1}$)
d_p	average carbon particle diameter (m)
k_f	external film transfer coefficient ($m \cdot s^{-1}$)
m_c	mass of carbon (kg)
m_s	mass of solution (kg)
n	empirical constant in Freundlich isotherm
V_s	volume of solution (m^3)
ρ	apparent density of carbon ($kg \cdot m^{-3}$)

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THE NATURE OF GOLD-IODIDE ADSORPTION ONTO COCONUT-SHELL CARBON

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ABSTRACT

With the increasing awareness of preserving the environment, the need for other lixiviants in leaching processes has escalated. The investigation for lixiviants, especially for gold, has entailed mostly the halogen group. From the halogens, iodine forms the most stable gold complex. It is the aim of this paper to investigate the nature of the gold adsorbed from iodine/iodide solutions onto the surface of a coconut type activated carbon. Experimental results indicated that the state of the gold on the carbon surface was dependent on factors such as pH and level of dissolved oxygen. The pH level influenced the potential of the specific solution and hence affected the reduction/oxidation properties of the activated carbon. At a low pH the general potential of the activated carbon remained too high to induce reduction of the gold-iodide complex, while at a high pH the solution potential dropped enough for the reduction of the gold complex. Oxygen acts as an oxidant with certain active sites on the carbon and the carbon itself, thereby inducing higher adsorption which leads to the reduction of the gold complex to elemental gold, even at low pH levels. Scanning electron microscopy indicated the presence of elemental gold on the surface of the carbon. Copyright © 1996 Elsevier Science Ltd

Keywords
Gold ores; activated carbon; redox reactions

INTRODUCTION

For the major part of this century cyanide has been the primary leaching agent for gold ore. It has good properties, such as its selectiveness for gold, and before activated carbon came on the scene it was also suitable for the recovery of gold by precipitation with zinc. Activated carbon has become a dominant adsorbent agent in the mining industry, especially for gold recovery. The mechanism of the adsorption of gold cyanide onto activated carbon has been investigated and published [1,2,3] widely. Gold cyanide easily adsorbs onto activated carbon and can be desorbed by various methods. However, in recent years, the use of cyanide has come under public scrutiny, especially on the environmental front. It is a hazardous reagent, particularly if operating in an acidic medium.

In view of the above, several researchers have been investigating alternative lixiviants, which include the halogen group [4,5,6,7,8]. From this group, iodine forms the most stable gold complex [1,9] in aqueous solutions, even up to a pH of 14. The dissolution of gold in an iodine/iodide solution is as follows.

Firstly, the principal oxidant, the tri-iodide ion is formed.

$$\mathrm{I_2(aq)} + \mathrm{I}^- \Leftrightarrow \mathrm{I_3}^- \tag{1}$$

This ion serves as an oxidant in the following electrochemical reactions.

$$\mathrm{Au} + 2\,\mathrm{I}^- \Rightarrow \mathrm{AuI_2}^- + e^- \textit{ (Anodic)} \tag{2}$$

$$\mathrm{Au} + 4\,\mathrm{I}^- \Rightarrow \mathrm{AuI_4}^- + 3\,e^- \textit{ (Anodic)} \tag{3}$$

$$\mathrm{I_3}^- + 2e^- \Leftrightarrow 3\mathrm{I}^- \textit{ (Cathodic)} \tag{4}$$

$$2\mathrm{Au} + \mathrm{I_3}^- + \mathrm{I}^- \Rightarrow 2\mathrm{AuI_2}^- \tag{5}$$

$$2\mathrm{Au} + 3\mathrm{I_3}^- \Rightarrow 2\mathrm{AuI_4}^- + \mathrm{I}^- \tag{6}$$

The rate of gold dissolution in a relative dilute iodine/iodide solution (5×10^{-3} M I_2 and 10^{-2} M NaI) is about the same as that for cyanide (2.7×10^{-3} M KCN and air) [8].

Studies [10,11,12,13] on the adsorption of gold chloride onto activated carbon indicated that gold chloride is adsorbed onto the carbon and is partly reduced and partly adsorbed in an acidic medium. The reduction of the gold chloride to the metallic state can be expressed by the following reaction :

$$4\mathrm{AuCl_4}^- + 2\mathrm{H_2O} + \mathrm{C} \Rightarrow 4\mathrm{Au} + 4\mathrm{HCl} + \mathrm{CO_2} + 4\mathrm{Cl}^- \tag{7}$$

Sun and Yen [13] concluded that the concentration of aqueous chlorine decreased the gold adsorption due to the redissolution of the gold from the carbon surface by the aqueous chlorine. Mensah-Biney *et al.* [14] concluded that gold bromide also reduces on the carbon surface (Reaction 8), simultaneous with the adsorption of the complex.

$$4\mathrm{AuBr_4}^- + 2\mathrm{H_2O} + \mathrm{C} \Rightarrow 4\mathrm{Au} + 4\mathrm{HBr} + \mathrm{CO_2} + 4\mathrm{Br}^- \tag{8}$$

An excess of bromine decreases the loading capacity of the carbon due to the oxidation of the carbon surface by the bromine, and hence prevents the adsorption of the gold bromide complex. Pesic and Storhoc [15] conclude, on the other hand, that gold bromide complex adsorbs only onto the carbon in its original ionic form.

The objective of this paper is to investigate and define the nature of gold that is found on the surface of a coconut shell activated carbon during adsorption of gold-iodide.

EXPERIMENTAL

All experiments were performed in an 1 L baffled batch reactor. Agitation was provided by a flat blade impeller, driven by a Heidolph variable speed motor. The impeller speed was kept constant at 300 rpm. Fine gold nuggets (1 g) were dissolved in an 1 L volumetric flask using 0.1 M KI and 5×10^{-3} M I_2 to obtain a 1000 ppm Au solution. All reagents used were of analytical grade and distilled water was used throughout. The pH was adjusted using either a 1 M HCl or 1 M KOH solution and was measured with a Beckmann Φ71 pH meter. The nitrogen and oxygen gases were supplied by Fedgas and the dissolved oxygen levels were measured with a Hanna HI 8043 dissolved oxygen meter. The potential of the solution was measured by the potential difference between a saturated (KCl) calomel electrode and a platinum or glassy carbon electrode with the aid of a TEST 2010 multimeter. All experiments were performed at room temperature.

All experiments were conducted at an initial gold concentration of 20 ppm which was in contact with 0.2 g of activated carbon. Equilibrium tests were performed over a period of two weeks. Samples were taken at regular intervals and the gold concentration was measured using a Varian AA-1275 atomic absorption spectrophotometer. The adsorbent used was a coconut shell activated carbon (average diameter of 1.4 mm) with a surface area of 1020 $m^2.g^{-1}$ and apparent density of 800 $kg.m^{-3}$, provided by ACIX (South Africa).

Scanning Electron Photographs were taken with an HITACHI S-405A Scanning Electron Microscope.

RESULTS AND DISCUSSIONS

Previous work [16] investigated the factors influencing the adsorption of gold–iodide onto activated carbon. It has been shown that concentrations of gold–iodide, iodine and tri-iodide influenced the adsorption characteristics of the system, while iodide concentration seemed to have no influence at all. Further experiments have shown that pH also affected the adsorption parameters. Furthermore, results have shown that at high pH levels, and at high concentrations of dissolved oxygen, elemental gold was formed on the surface of the carbon.

The main species that adsorb on the carbon surface from the solution are iodine [17], iodide [18], gold(I) iodide and gold(III) iodide complexes. The potential difference between a saturated calomel electrode and a platinum or glassy carbon electrode in the solution was measured (Table 1). Marsh [19] stated that glassy carbon electrode can be used as a substitute for an activated carbon electrode due to the structural similarities between the two types of carbon.

TABLE 1 Potential of gold–iodide solutions at different pH levels—saturated calomel (KCl) vs. platinum or glassy carbon (G.C.) electrode

Time	pH 2		pH 6.5		pH 11	
Days	mV		mV		mV	
	G.C.	Pt	G.C.	Pt	G.C.	Pt
0	636.5	636.5	640.5	641.5	550.5	no readings
0.3	615.5	617.5	617.5	620.5	488.5	taken
1	571.5	633.5	491.5	587.5	399.5	
2	571.5	581.5	486.5	574.5	353.5	
3	567.5	582.5	477.5	569.5	341.5	
4	567.5	581.5	472.5	569.5	271.5	
5	567.5	582.5	472.5	569.5	271	
6					269.5	
7					271.5	
8					271	

Combining the E values obtained (Table 1) with the relevant Pourbaux diagrams for the solutions (Figure 1 (Eh–pH gold–iodide/water system); and Figure 2 (iodide/water system), it is possible to determine the predominant species present in the solution at a certain time. In Figure 1 it can be clearly seen that at pH 2 and 6.5, the principal species are AuI_2^- and AuI_4^-, while at pH 11 it drops into the area where elemental gold is predominant. Figure 2 shows that at pH 2 the dominant iodine species is tri-iodide, which, as explained earlier, is the predominant oxidation agent in the solution. At pH 6.5 the potential of the solution drops further into the area where the iodide ion is predominant. This clarifies that, even in Figure 1, where the potential did not drop into the elemental gold area, the small amount of gold that is reduced on the activated carbon surface is not redissolved by the I_3^- ion. At pH 11, the predominant gold species becomes elemental gold and the [I_3^-] is nearly non-existent, so that none of the reduced gold is redissolved. Electroscanning Micrographs (Figures 3-7) highlight these elemental gold deposits on the carbon surface.

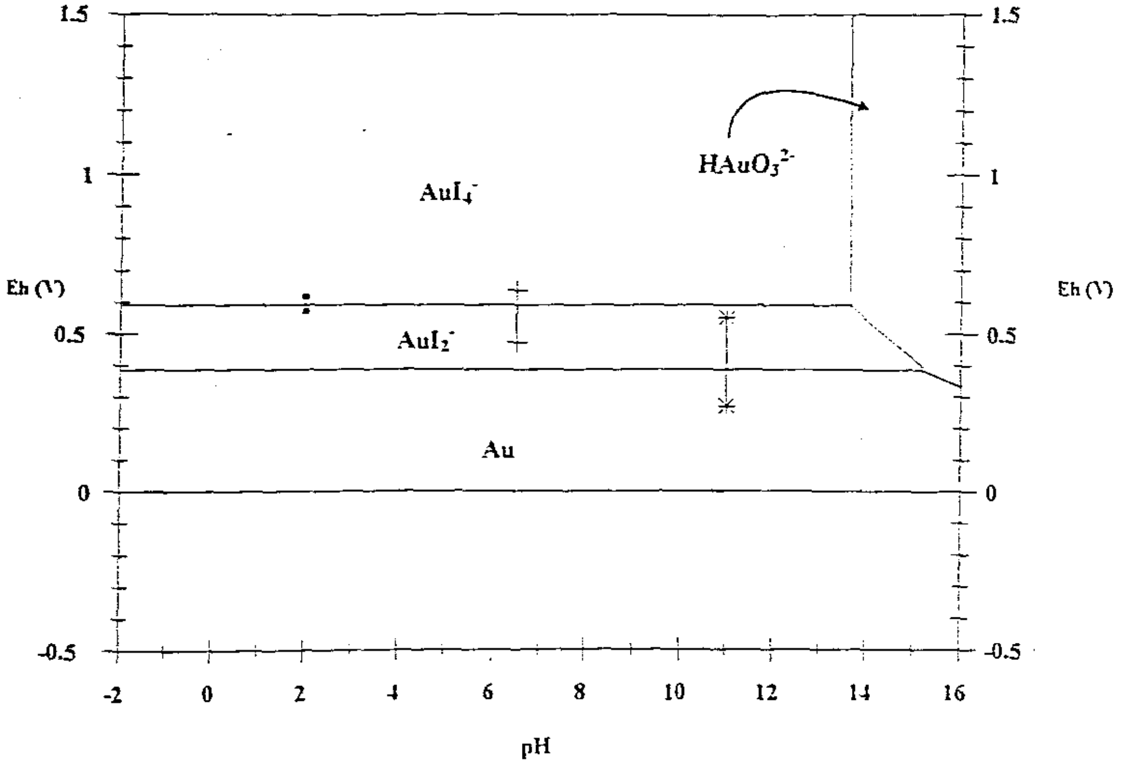


Fig.1 Eh-pH equilibrium diagram for gold-iodide/water system [Au] = 10^{-5} M and $[I^-]$ = 1 M

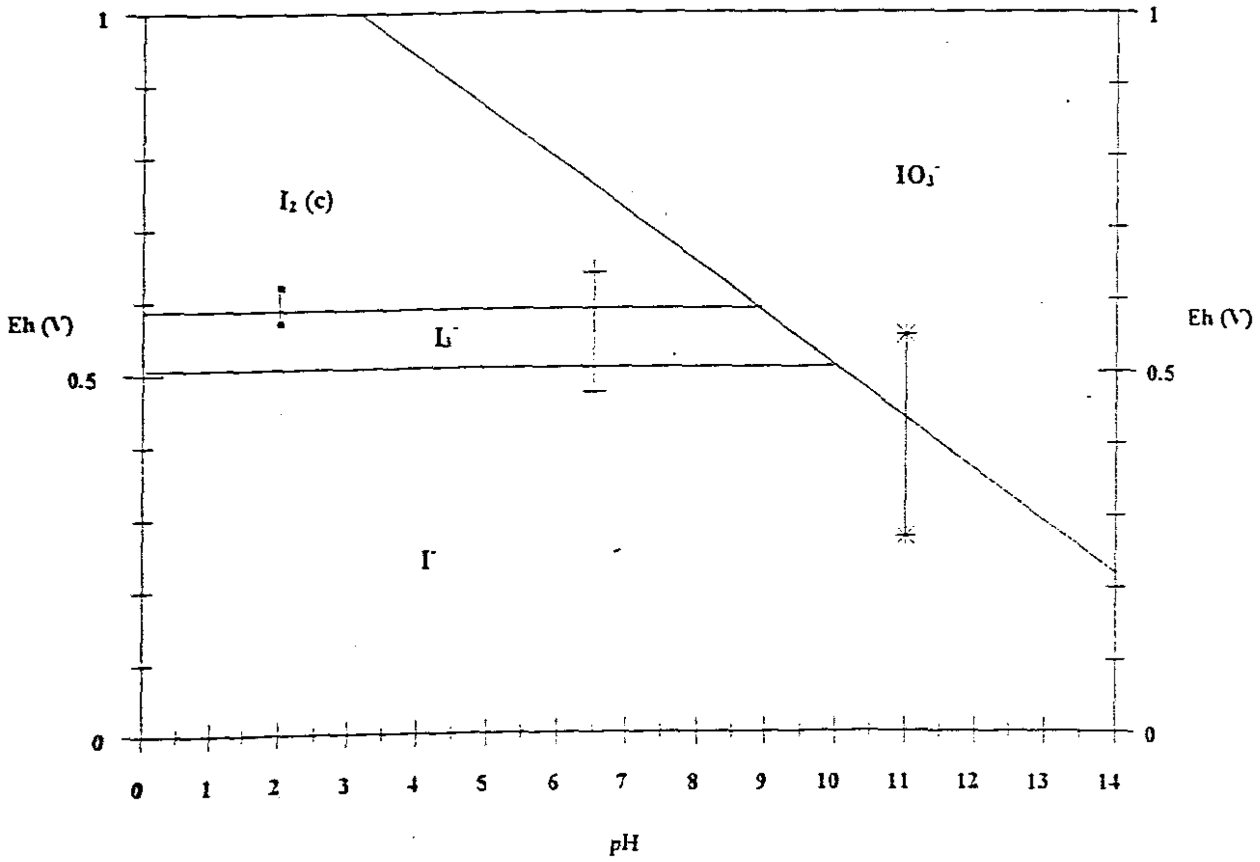


Fig.2 Eh-pH equilibrium diagram for iodide/water system $[I^-]$ = 1 M

The electrochemistry involved in the reduction of the gold-iodide complex is combined in the next set of

$$AuI_4^- + 3e^- \Leftrightarrow Au + 4I^- \qquad E_o = 0.57\ V \tag{9}$$

$$AuI_2^- + e^- \Leftrightarrow Au + 2I^- \qquad E_o = 0.57\ V \tag{10}$$

$$CO_2 + 4H^+ + 4e^- \Leftrightarrow C + 2H_2O \qquad E_c \tag{11}$$

$$4AuI_4^- + 3C + 6H_2O \Rightarrow 4Au + 3CO_2 + 12H^+ + 16I^- \tag{12}$$

$$4AuI_2^- + C + 2H_2O \Rightarrow 4Au + CO_2 + 4H^+ + 8I^- \tag{13}$$

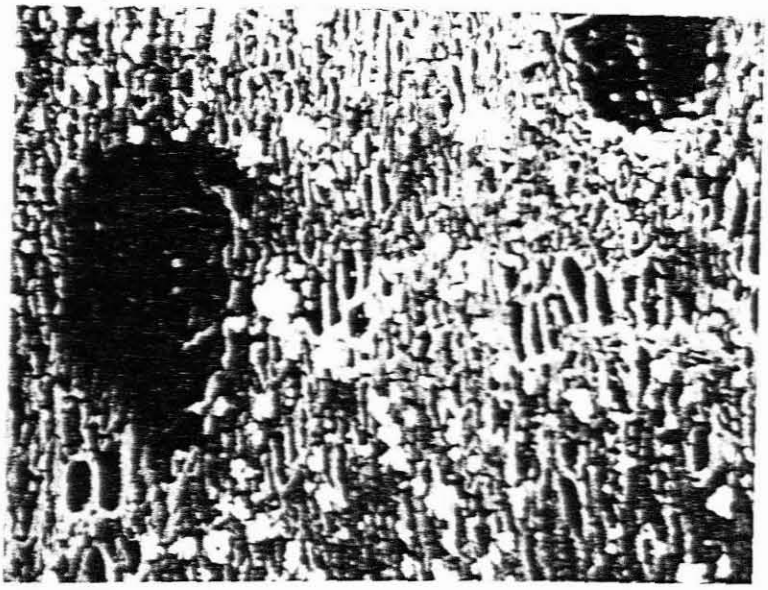


Fig.3 Electron scanning micrograph of activated carbon surface after 2 week contact with 20 ppm. gold–iodide solution at pH 6.5 (Magnified x 1000)

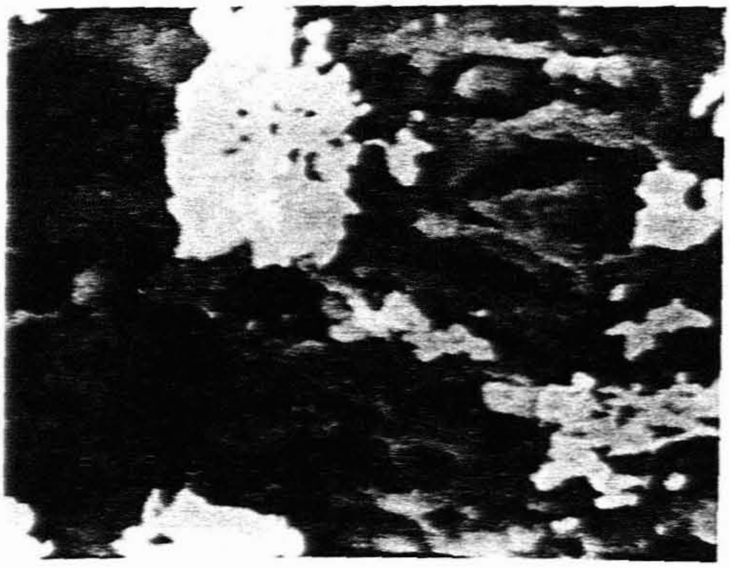


Fig.4 Electron scanning micrograph of activated carbon surface after 2 week contact with 20 ppm. gold–iodide solution at pH 6.5 (Magnified x 2000)

For reduction/cementation of the gold complex to take place at the carbon surface, the result of Equation 14 must be negative

$$E_o - E_c = \Delta E. \tag{14}$$

Jankowska *et al.* [18] investigated the electrochemical properties of activated carbon and concluded that the potential of activated carbon is related to the kind of anion species present in the solution, and that the potential decreases with an increase in concentration of the electrolyte. This effect on the activated carbon potential was the strongest for solutions containing iodide ions. Also, the carbon potential (E_c) changes as the pH of the solution changes. Thus, to calculate the approximate correct potential for Reaction (11) the Nerst equation can be derived to:

$$E = E_c - 0.059 \cdot \mathrm{pH}\ (\mathrm{V}) \qquad \text{at } T = 25^\circ\mathrm{C} \tag{15}$$

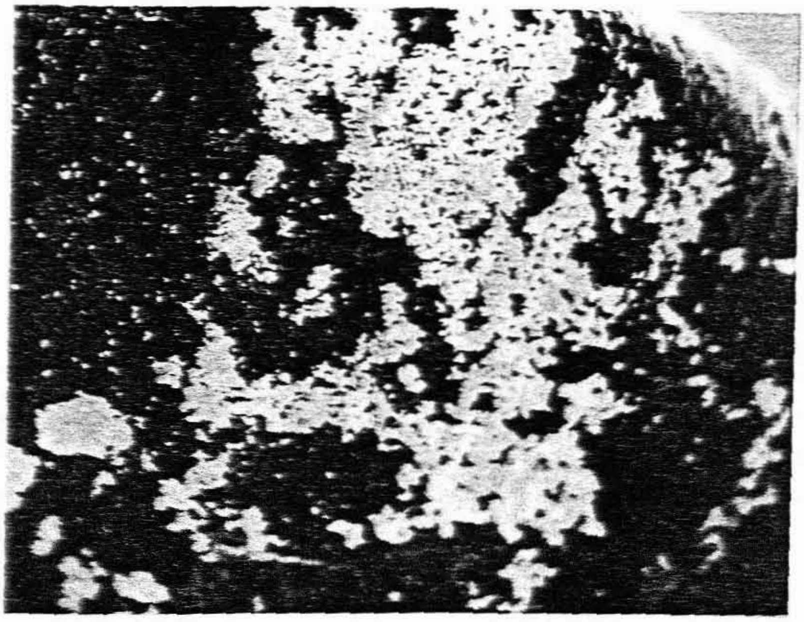


Fig.5 Electron scanning micrograph of activated carbon surface after 2 week contact with 20 ppm. gold-iodide solution at pH 11 (Magnified x 100)

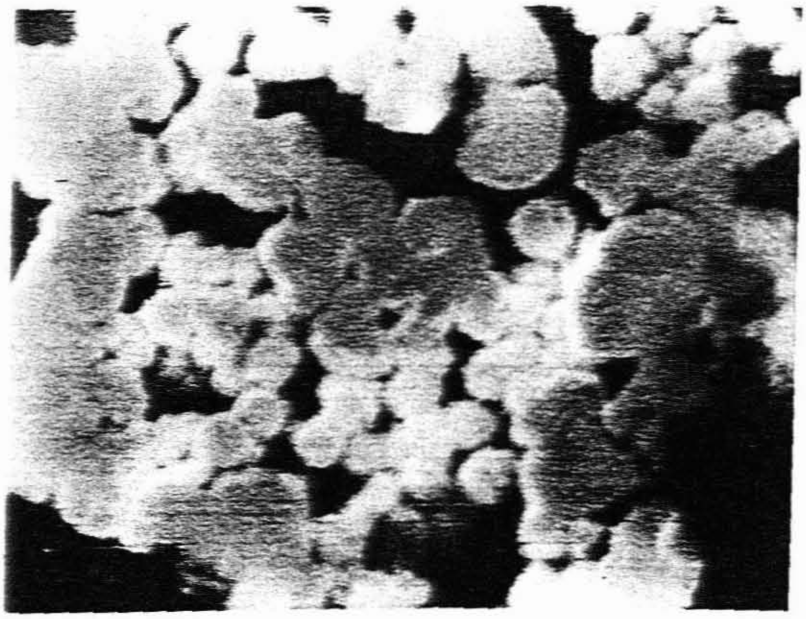
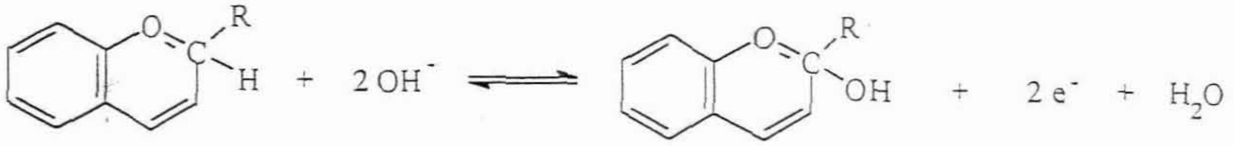


Fig.6 Electron scanning micrograph of activated carbon surface after 2 week contact with 20 ppm. gold-iodide solution at pH 11 (Magnified x 2000)

Some of the active groups identified [20] on the carbon surface are quinone and chromene groups (Reactions 16 and 17). Therefore, these groups could be oxidised to form an electrochemical reaction with the gold-iodide, and using Eq. 15 it can be determined that reduction of gold-iodide can take place from pH 2.19 upwards.

E = 0.699 V (16)



(17)

The carbon surface contains more active groups than those mentioned, but most of them are not quantified as yet.

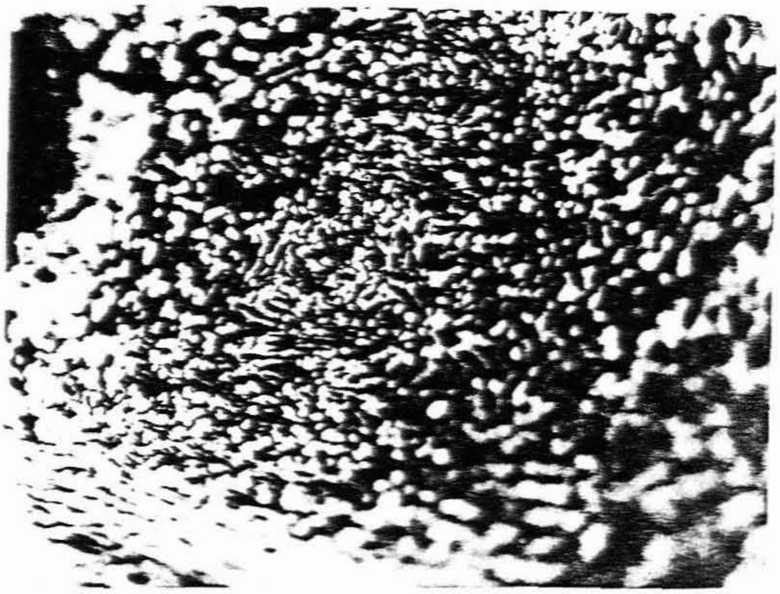


Fig.7 Electron scanning micrograph of activated carbon surface after 2 week contact with 20 ppm. gold-iodide solution at pH 6.5 and [dissolved oxygen] of 32 ppm. (Magnified x 100)

Dissolved oxygen oxidises Reactions 16 and 17 as well as other active sites on the surface of the carbon [20] and thereby enhances the gold adsorption in combination with the reduction of the gold complex to natural gold.

Baba *et al.* [17] analysed the adsorption of iodine on activated carbon and concluded that iodide species hardly adsorb on activated carbon. This contradicts Jankowska *et al.* [18] who indicated that iodide adsorbed readily. Previous work [16] indicated that iodide concentration did not influence the equilibrium nor kinetics of the gold-iodide adsorption. Therefore, during the adsorption process, iodine is a competitive reactant for adsorption with the gold complex.

CONCLUSION

Gold–iodide can be found on activated carbon in two principal states, namely an ionic form and an elemental state. Dissolved oxygen and pH are the major factors influencing the nature of the gold on the surface of the carbon. Dissolved oxygen adsorbs onto the activated carbon surface and oxidises certain functional groups, thereby enhancing the adsorption and reduction of the gold-iodide on the activated carbon surface. This oxidation process contributes electrons towards the reduction of the gold complex. This can take place from a pH of 1.89 and higher.

When the pH level is low, the principal species in the solution is AuI_2^- and I_3^-. Thus, any gold reduced by oxygen will be redissolved by tri-iodide. When the pH level rises, the potential of the solution drops, and the predominant gold species in solution tend to change towards elemental gold while iodine species tend towards iodide. Therefore, the gold complex easily reduces onto the carbon surface to natural gold. At high pH levels, tri-iodide is not present in the solution, and gold does not re-dissolve from the carbon surface.

NOMENCLATURE

E = approximate potential of activated carbon
E_o = half cell reaction potential
E_c = half cell potential for activated carbon functional group

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