SCREENING OF TECHNOLOGIES FOR THE RECOVERY OF RHODIUM(III) METAL IONS FROM A PRECIOUS METAL REFINERY WASTEWATER

A thesis submitted in fulfilment of the requirements for the degree of

Master of Science (Biotechnology)

Of

Rhodes University

By

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January 2005

ABSTRACT

The selective recovery of rhodium from wastewaters, in which the metal would otherwise be lost, would be highly profitable if the process were suitably low-cost. Current recovery processes are generally high maintenance and high-cost, whereas biological processes can be engineered to run with little external input in terms of cost and maintenance.

Three emerging technologies were chosen based on their reported efficiency when removing base metals from wastewaters. The first technology screened, the sulphide-extraction membrane bioreactor (SEMB), consists of a sulphate-reducing prokaryote (SRP) anaerobic digester, in which a silicone membrane is submerged. Wastewater is passed through the membrane and metal ions are precipitated as metal sulphides by the hydrogen sulphide gas, which is capable of permeating the membrane. The second technology screened was a fluidized sand bed reactor in which metal ions are removed from solution via induction of nucleated precipitation by sodium carbonate onto the sand grains. The third, and most well established removal technology screened was a biosorption system using immobilized *Saccharomyces cerevisiae* biomass as the biosorbent. Experimental trials with each technology highlighted drawbacks with each; the SEMB system proved to be largely ineffective when challenged with the removal of rhodium from the wastewater as the rhodium precipitate fouled the membrane within hours, the fluidized bed system seemed unable to overcome the acidity of the wastewater and thus could not precipitate out the rhodium metal, and the efficiency of the biosorption process was hampered by the diversity of rhodium species present in the wastewater, which reduced the amount recovered.

The outcomes of the trials with each technology indicated that further optimization of the technology or pretreatment of the wastewater is necessary before any of these options can be implemented. It could be concluded, however, that despite further optimization, both the SEMB and the fluidized bed system were not applicable in this case as precipitation would be non-specific, resulting in the necessity for further steps in order to purify the rhodium ions. Hence, the biosorption system was shown to be most applicable, and further optimization of the system could yield a highly efficient rhodium recovery process.

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LIST OF ABBREVIATIONS

A	Effective membrane surface area (m^2)
AAS	Atomic absorption spectrophotometer
AB	Acetogenic bacteria
AMD	Acid mine drainage
ANOVA	Analysis of variance
APS	Adenosine-5’-phosphosulphate
B	Affinity coefficient
BIC	Bushveld igneous complex
BOD	Biological oxygen demand
C_f	Metal concentration in aqueous solution at equilibrium
CMDTC	bis(carboxymethyl)dithiocarbamate
COD	Chemical oxygen demand
$C_{r,t}$	H2S concentration in aqueous solution in the receiving water (mol/m^3)
$C_{s,o}$	Initial H_2S concentration in aqueous solution in the supernatant (mol/m^3)
$C_{s,t}$	H_2S concentration in aqueous solution in the supernatant (mol/m^3)
CWT	Centralized waste treatment
Df	Degrees of freedom
DOC	Dissolved organic carbon
DT	Distillation
DWAF	Department of Water Affairs and Forestry
EDTA	Ethylenediamine tetraacetic acid
EMBR	Extractive membrane bioreactor
EMBR-SRP	Extractive membrane bioreactor-sulphate-reducing prokaryote
ENPAT	Environmental potential atlas
FBR	Fluidized bed reactor
GA	Glutaraldehyde
GAC	Granulated activated carbon
HDEHP	bis(2-ethylhexyl)phosphoric acid
HRT	Hydraulic retention time
HSAB	Hard and soft acid and base
IX	Ion exchange
k_{ov}	Overall mass transfer coefficient (m/s)
MABR	Membrane aeration bioreactor
MB	Methanogenic bacteria
MBR	Membrane bioreactor
MiBK	Methly isobutyl ketone
MS	Mean square

N	Flux across membrane (mol/sec/m^2)
NO$_x$	Nitrogen oxides
PAPS	Phosphoadenosine-5'-phosphosulphate
PEI	Polyethylenimine
PGEs	Platinum group elements
PGMs	Platinum group metals
PMR	Precious metal refinery
PVDF	Polyvinyl fluoride film
Q	Metal uptake (mg metal/g biosorbent)
Q_{max}	Maximum metal uptake (mg metal/g biosorbent)
SAM	Subsequent addition method
SD	Standard deviation
SEMB	Sulphide-extraction membrane bioreactor
SIR	Solvent impregnated resins
SLM	Supported liquid membrane
SRB	Sulphate-reducing bacteria
SRP	Sulphate-reducing prokaryotes
SS	Suspended solids
SS	Sums of squares
SX	Solvent extraction
T	Time (s)
TMP	Transmembrane pressure
TOA	Tri-*n*-octylamine
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UG2	Upper group 2
V	Volume of supernatant used (m^3)
VSS	Volatile suspended solids
XAD-4	Polystyrene-divinylbenzene

ACKNOWLEDGEMENTS

A number of people have been especially patient with me over the last two years and I would like to take this opportunity to thank them for their unwavering support and friendship throughout my time at Rhodes.

- Dr Jo Burgess. My supervisor when I needed one, and my friend when I just needed to talk.
- My lab mates in 129A and C for their patience and understanding when things became frantic.
- The departmental staff and students, who provided many hours of wonderful diversion.
- Mike, Doug, Henry and Vuyo, for all, at one time or another, letting me know that life does get better after a Masters degree.
- To my favourite "Hoeries", Nuraan, Greer and Rory, thanks for the good nights I will always remember, and for those that I simply can't.
- My favourite "favourite", Hylton, for the love and support that kept me focussed on the final outcome of the past two years.
- My family, without whom I would not be where I am today. Thank you for providing me with the emotional and financial support I needed to get this far, and for a wonderful place to escape to when the pressure became too much and I just needed a break.
- Ms Kerry Slatter and Dr Dave Robinson, representatives of my industrial sponsor, thanks for all of your interest and input into my research.
- The financial assistance of the Department of Labour (DoL) is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author, and are not necessarily to be attributed to the DoL.
- The NRF.

CHAPTER 1

LITERATURE REVIEW

1.1 WATER: A RENEWABLE RESOURCE

Water is an important resource, vital for both social and economic growth. It is thus imperative that water is managed according to the principles of sustainable development to counteract the combination of increasing economic development and environmental degradation. The constantly increasing degree of industrialization and urbanization, rising standard of living, increasing population growth and agricultural activities are strongly impacting on the use of available water sources and on the quality of water that is found therein. This exhaustive use of limited resources and energy by modern society implies a need for changes in present and future urban water and wastewater treatment systems (Holtzhausen, 2002).

A larger problem faces developing countries, like South Africa, that have moderate to high stresses on their freshwater resources, as large inequalities exist in the quality and quantity of water available to rural communities compared to that of the urban areas (Morrison *et al.*, 2001). Thus, appropriate management strategies need to be implemented to optimize the use of these water sources and the efficient disposal of polluted water (Jooste, 2000).

South Africa's average annual rainfall is approximately 480 mm - almost half the world average of 860 mm. The fact that this rainfall is unevenly distributed across the country, much higher in the east than in the west, compounds the problem of water supply (Holtzhausen, 2002). Major industries, mining and power generators account for a large percentage of water usage in South Africa. These are found mainly in Gauteng, Mpumalanga and Limpopo provinces, which are highly populated, due in part to the labour force required to run such industries and the resulting commercial and residential areas surrounding them. The result is a very high water demand by both industrial and domestic users in an area of generally low rainfall (Figure 1.1) (Holtzhausen, 2002).

To alleviate this inequality between the eastern and western areas of the country, numerous dams, storage facilities and inter-catchment transfer schemes have been developed. Thus, South Africa is heavily reliant on surface water resources and with evaporation rates much higher in the west than in the east, the potential water shortage problem is evident (Webster, 2001).

In combination with the two water-related issues of increasing urbanization and uneven resource distribution, the need for sufficient water to sustain aquatic ecosystems and the environmental services they provide results in a requirement for a fine balance when it comes to allocating resources to users. Schutte and Pretorius (1997) state that of the total water resource presently available, 52 % is used in agricultural activities, 12.5 % by industry, mining and power generation and 12 % for domestic and municipal uses. Holtzhausen (2002) echoes these consumption estimates and further states that at least 15 % of the water resources remaining are required for nature conservation and ecological purposes such as maintaining estuaries and rivers (Figure 1.2).

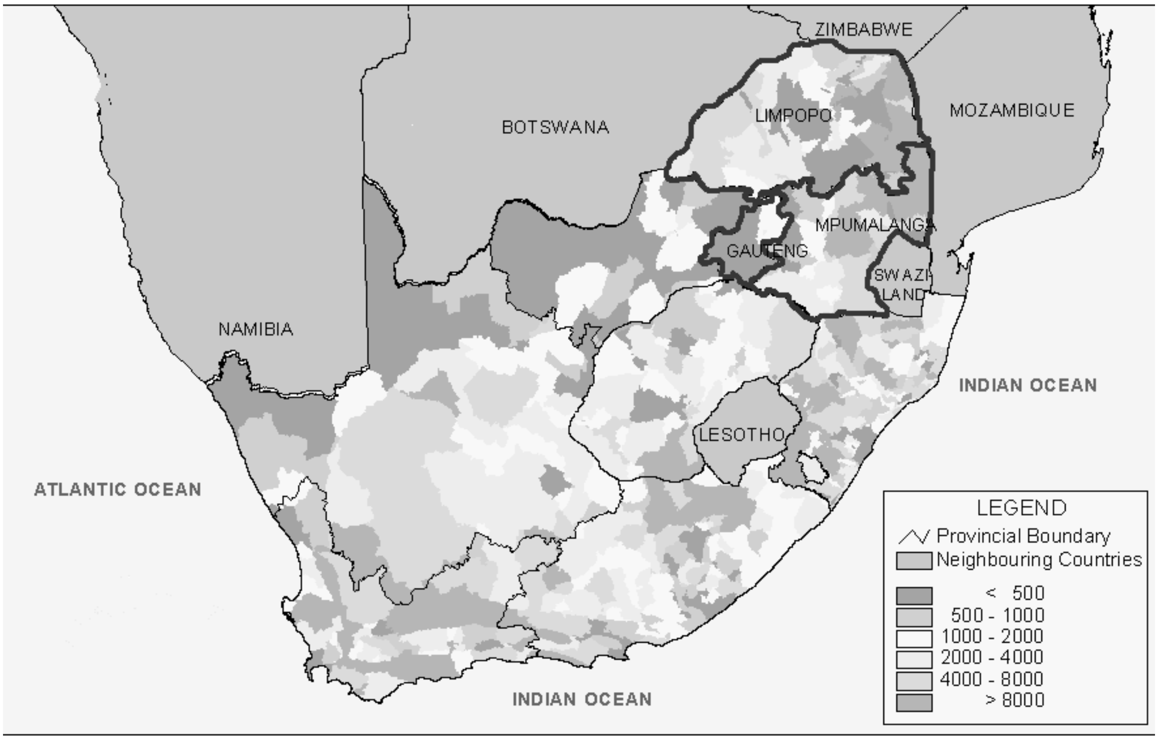


Figure 1.1 Availability of water per capita in South Africa (Environmental Potential Atlas (ENPAT), Department of Environmental Affairs and Tourism, South Africa, Internet Ref.1).

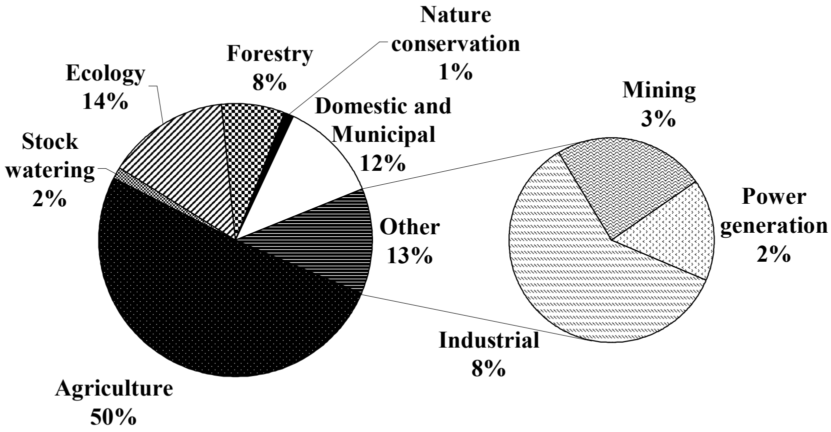


Figure 1.2 Current sectoral consumption of available water resources (Holtzhausen, 2002; Schutte and Pretorius, 1997).

This need has been recognized in the national legislation under the National Water Act (1998) that outlines three policy principles for water resource protection strategies. These are:

- Protection of all significant water resources.
- Resource sustainability, i.e. use that does not cause long-term deterioration of the overall resource in terms of any measurable criteria (e.g. quality and quantity) (Wright and Xu, 2000).
- Integrated water resource management of all water user groups.

It is the third principle that places pressure on all industries to reconsider their current water management strategies and look for ways to increase the amount of reuse and recycling that occurs within that industry.

1.1.1 WATER IN INDUSTRY

The most widely used raw material in process industries, as well as an abundant component of chemical, petrochemical, petroleum refining, food and drink, pulp and paper and many other industries is water (Baetens, 2002). In light of the potentially chronic water shortage facing South Africa, awareness and motivation among the larger users for optimization of water utilization is increasing. This increase is as a result of powerful economic driving forces such as increased cost of wastewater treatment, higher environmental standards and the increasing scarcity and cost of good quality water sources (Alva-Argáez *et al.*, 1998).

Water use minimisation can be achieved in three basic ways:

- Reduction in the use of fresh water by instituting changes in the process (Zhelev and Bhaw, 2000; Alva-Argáez *et al.*, 1998).
- Reuse of process water in areas where high quality water is not key and lower water quality will not adversely affect the process into which it is being added (Pulles *et al.*, 1996).
- Reduction in water treatment costs by implementing low-cost biological treatments and reusing this treated water (Alva-Argáez *et al.*, 1998; Pulles *et al.*, 1996).

The third option can be further split into regeneration reuse and regeneration recycling. The first involves partial recycling to remove contaminants that may affect the process into which the water is being added. Regeneration recycling requires that the treatment remove any contaminants that may build up, as the treated water will pass through the same process from which it was taken (Zhelev and Bhaw, 2000).

South African industries are experiencing increasing international pressure to reduce the amount of freshwater used and the amount of effluent produced. A technique known as water pinch analysis is gaining in popularity as a ‘cleaner production’ technique aimed at reducing freshwater consumption and wastewater production by analyzing current or proposed industrial complexes and pinpointing areas where changes such as those mentioned earlier can be implemented (Gianadda *et al.*, 2002; Zhelev and Bhaw, 2000). In South Africa, the Pollution Research Group at the University of KwaZulu-Natal have been at the forefront of water pinch analysis implementation by aiding diverse industries in the analysis of their own water usage and highlighting the possibilities for change (Brouckaert *et al.*, 2002).

Industries involving the extraction, purification and application of metals are generally highly water-intensive. For example, in 2002, a Water Research Commission study estimated that the electroplating industry produced approximately 1 cubic kilometer of liquid effluent per annum globally (Swalaha *et al*., 2002). Effluent streams released by these industries are characterized by contaminants such as cyanides, heavy metals, associated salts, oils and greases, cleaning aids and solvents (Cowan, 1998). These contaminants arise, in one way or another, from processes within the industry and, depending on the process, the reclamation of components such as organic solvents and metals from these waste streams may be financially viable. The major factors used to determine the financial viability of reclamation include the volume of water that contains metals, the concentrations of those metals in the water and the potential to recirculate some of the metal salts and recovered waters as opposed to discharge fees and penalties (Cowan, 1998).

For industries such as electroplaters and finishers, the cost involved in treatment of effluent produced is sometimes prohibitively expensive, especially for the smaller installations, and far outweighs the advantages of recycling and regeneration of materials. Cowan (1998) suggests that centralized waste treatment (CWT) plants be set up to provide such services for a number of small industries in a given area, which would lower capital costs and still produce the advantages inherent in the idea. For mines and metal refiners however, the possibility of retaining every milligram of metal value is highly attractive and the increase in profit gained by the extra metal value will soon outweigh the cost of the treatment plant installation. Present treatment strategies require costly chemical and physical operations and involve a high degree of maintenance and operating supervision. Reliable treatment systems that are cost-effective and low maintenance would be an ideal solution for these mines and metal refiners.

Precious metal refineries have the most to gain from maximizing their metal recovery efficiencies. The value of the metal retained rather than lost to a slimes dam would rapidly repay the initial capital outlay required for the installation of a metal recovery plant. Rhodium, in particular, is the least efficiently refined metal, with a significant percentage (when compared to other PGMs) of the metal value being lost due to the inefficiency of the extraction technique (Benguerel *et al*., 1996). In light of this and the fact that the applicability of rhodium is growing rapidly, recovery of this metal from refinery wastewater is becoming increasingly worthwhile.

At present, rhodium finds its major application in the autocatalyst industry, where it provides the major catalytic surface for the conversion of noxious exhaust fumes to non-toxic gases, suitable for emission into the environment. This industry makes up 84 % of the annual rhodium demand (Johnson-Matthey, 2003). Other applications include the chemicals, glass and electrical industries, where its hardness makes it an excellent alloying agent to harden platinum. This hardness, along with its high melting point, high temperature stability and corrosion resistance, makes it key to many industrial processes such as glass, glass fibre and nitric acid production (Johnson-Matthey, 2003).

1.2 CLASSICAL METHODS OF METAL REMOVAL FROM WASTEWATER

The recovery of metals from wastewater has a twofold advantage. Firstly, it minimises the contamination of the aquatic environment and secondly, recovering metals of value such as gold and platinum group metals (PGMs) would have significant commercial value (Volesky, 1990). According to convention, the majority of current metal removal and recovery technologies are physical or chemical in nature. Biological systems however, are gaining in popularity, as they are more and more being proved to be as effective as the physical methods while operating at substantially lower cost (Eccles, 1999). Membrane systems are still being developed and most potential applications involve the use of membranes as either filtration devices (Juang and Shiau, 2000) or as metal ion chelators in combination with other adsorbent material (Genç *et al*., 2003).

Metal accumulation tends to be a function of the metal concentration. Where metals are in high concentrations (> 500 mg/L), they can be recovered by electrolysis, while at low concentrations (< 5 mg/L), they can be removed by biosorption or ion exchange. At concentrations between 500 and 5 mg/L, precipitation with lime is possible, generating high volumes of sludge with low metal/sludge ratios (Diels *et al*., 1993)

1.2.1 METAL REMOVAL METHODS AVAILABLE

There are a number of strategies available for the removal of metal ions from wastewaters. These include cementation, solvent extraction, evaporation, ion exchange, chemical precipitation, biological treatment and membrane processing.

The application of cementation reactions in industry has attracted attention over the past century. This technology has found application in recovering silver from industrial baths used for electro winning or electro refining of copper (Sulka and Jaskuła, 2003). The principle of cementation is the contact between the metal in solution and a metal of a higher electronegativity series. This causes the displacement of the metal from solution (Lee *et al*., 1998).

Solvent extraction, or liquid ion exchange, involves extracting the metal of interest by contacting the solution with an organic reagent that will react with the metal ion and result in its conversion to a form soluble in the solvent. In metal wastewater remediation, solvent extraction is well established. For optimal operation, this method requires high initial metal concentrations (Kentish and Stevens, 2001). However, the environmental standards for acceptable metal levels in discharged water cannot be met with this method alone. It is preferable to utilize it in conjunction with other treatment systems such as membranes (Kentish and Stevens, 2001; Kapoor and Viraraghavan, 1995). Solvent extraction of metals is widely employed for selective recovery. It is one of the most common methods used for the separation of PGMs from aqueous solutions due to the simplicity of the process (Gholivand and Nozari, 2000). The precious metal anions are usually extracted by ion-pair formation with long-chain alkyl amines such as tri-n-octylamine (TOA), methyl tricaprylyl ammonium chloride (Aliquot 336), methyl isobutyl ketone (MiBK) and other amines (Adams, 2003; Kentish and Stevens, 2001).

Mining operations may “treat” metal-contaminated waters using atmospheric evaporation of the water, which causes a concentrated metal-bearing sludge to be formed. The dams required for this method can occupy vast areas of land, making it a viable option only for processes where this land is available close by. Vacuum evaporation, in which the water is vaporized at low temperatures, is only occasionally employed, as the equipment required is complex and expensive to construct and maintain (Cowan, 1998).

The use of ion exchange resins results in highly successful metal recovery from pretreated waste. Conventional ion exchange resins have been used in conjunction with solvent extraction in the recovery of metals. The ease of phase separation and high concentration efficiency of ion exchange mask the disadvantages of solvent extraction, mainly the difficulty in phase separation (Adams, 2003). These ion exchangers are no longer sufficiently selective to remove certain metals from large volumes of accompanying metals and metal-selective resins are being developed (Cortina *et al*., 1998). However, these methods are relatively expensive with elaborate equipment, high operation costs and energy requirements and a major cost is the regeneration and/or disposal of the resin regeneration liquid and the spent resin itself. These also represent a large environmental burden in terms of disposal (Lee *et al*., 1998). Table 1.1 summarizes the major performance characteristics of some of the physico-chemical methods used commercially.

There is a global trend moving towards more stringent environmental standards and legislation. The current economic climate encourages the introduction of relatively low-cost pollution treatment systems. The benefits of natural systems are becoming more apparent as a greater number are successfully implemented. These natural systems are often referred to as “green” technologies as they involve naturally occurring biological phenomena and systems. Two important phenomena, biosorption and bioaccumulation, are implicated in the removal of metal ions from wastewater in all biological systems. These can occur in both plant and microbial species. Bioaccumulation is an active process, whereby the biomass transports the metal ions into the cells where the metal is then sequestered. The disadvantage of this process is that the concentration of the metal may reach a level that is toxic to the organism, and kill it. Biosorption is a passive process, in which the metal adsorbs to functional groups on the outer surface of the biomass. This process can occur on both living and dead biomass and thus, the limiting factor is the availability of binding sites onto which the metal can adsorb (Volesky, 1990).

Table 1.1 Performance characteristics of some physico-chemical heavy metal removal and recovery technologies (Eccles, 1999).

Technology	**Performance characteristics**				
	pH change	**Metal selectivity**	**Influence of suspended solids**	**Tolerance to organic molecules**	**Working level for appropriate metal (mg/l)**
Adsorption (e.g. GAC*)	Limited tolerance	Moderate	Fouled	Can be poisoned	< 10
Electrochemical	Tolerant	Moderate	Can be engineered to tolerate	Can be accommodated	> 10
Ion exchange	Limited tolerance	Chelate resins can be selective	Fouled	Can be poisoned	< 100
Precipitation as hydroxide	Tolerant	Nonselective	Tolerant	Tolerant	> 10
Solvent extraction	Some systems tolerant	Metal-selective extractants available	Fouled	Intolerant	> 100

*Granulated activated carbon

Membrane processes involving the removal of heavy metals from solution are presently limited to those that require a membrane as a pretreatment filtration device linked to a chemical, physical or biological removal process. An example of this is a combination of membrane technology and solvent extraction suggested by Kentish and Stevens (2001) in metal removal from industrial wastewater. In this example, the membrane is placed between the waste stream and the solvent stream and mass transfer of the selected chemical species occurs across the membrane into the solvent.

Chemical precipitation is the simplest and cheapest means of removing most heavy metals from solution (Cowan, 1998). This is mostly achieved by increasing the pH of the effluent, thereby precipitating the metal in an insoluble form, usually its hydroxide (Eccles, 1999). Hydroxide sludges are preferred to sulphide sludges, because the sulphide can make reclamation difficult. In addition, problems exist in terms of the health and safety issues surrounding the handling of chemical sulphide. These include the odour, toxicity and corrosive nature of the gas. Sodium hydroxide is also the best-favoured alkali as it introduces the smallest amount of inert material to the sludge (Cowan, 1998). In the long-term though, this becomes expensive, as large volumes of effluent must be treated daily and large volumes of metal-laden sludge are produced (van Hille *et al.*, 1999). For example, the precipitation of 100 mg/L copper(II) produces as much as 1000 mg/L sludge (Eccles, 1999). Traditionally hydroxide precipitants such as lime and caustic soda are favoured over their sulphide counterparts due to the much higher cost of chemically produced H_2S and the hazards associated with its manipulation (Cowan, 1998).

1.3 RECOVERY OF PRECIOUS METALS

As a result of the poor availability of novel process data for the biological recovery of precious metals from aqueous wastewaters, three technologies were chosen as potential rhodium recovery processes based on their novelty and apparent success in terms of recovery of base metals.

Sulphide precipitation of metal ions is by no means a new technology, but its combination with a membrane bioreactor system is an extremely exciting alternative technology for the bioremediation of wastewater (Livingston *et al.*, 1998), despite the lack of published data regarding its efficiency when used to recover precious metals.

Chemical precipitation is one of the most common conventional techniques for metal removal from industrial wastewaters. However, the disadvantages inherent in the process limit its overall efficiency. The compaction of the precipitation and settling process into a single fluidised sand bed reactor system offer enormous advantages over the conventional process. Again, no data are available regarding precious metal recovery using nucleated precipitation, but base metal results show this technology to be a promising one (Lee *et al.*, 2004; Zhou *et al.*, 1999).

The use of biomass as adsorbents for the removal of metal ions from aqueous solutions has been a topic of great interest for a number of years. Although the technique is not new, the constant screening of new materials to be used in such processes results in a growing pool of biosorbents from which to choose. A small number were compared by Vegliò and Beolchini (1997).

Large volumes of published data exist regarding the recovery or removal of base metals from aqueous solutions. The same cannot be said for precious metal recovery. With regard to the present studies, choices were made regarding the technologies to be used based on their efficacy in extracting base metals from solution. However, in most cases these technologies require large-scale reoptimization before similar high removal efficiencies are recorded for precious metals. This is largely due to the solution chemistry of precious metals being generally very different to that of base metals. For example, in biosorption processes, anions are typically adsorbed at low pH (1 –3) (e.g. pH 1.6 – 1.8 for platinum and palladium (Godlewska-Zyłkiewicz, 2003)) and cations at higher pH (4-7) (e.g. pH 5.0 for lead and copper, and pH 5.5 for cadmium, zinc and nickel (Sheng *et al.*, 2004).

In wastewaters with high chloride concentrations and typically low pH, such as PGM refinery wastewaters, PGMs are present in the form of anionic chloro-complexes with complicated solution chemistry, where the species composition is dependent on factors such as chloride concentration, pH, ionic strength, temperature, and, especially in the case of rhodium, the age of the solution (Benguerel *et al.*, 1996). To further complicate the recovery technologies chosen, the different species present react differently to the extraction process applied.

1.4 SULPHATE REDUCING PROKARYOTES AND MEMBRANE BIOREACTORS

1.4.1 SULPHIDE PRECIPITATION OF METALS

Despite the disadvantages, there are a number of countering advantages to using sulphide as a precipitant. One is the production of lower sludge volumes compared to hydroxide precipitation (Kaksonen *et al.*, 2003; Cowan, 1998). This has huge financial impacts on waste management strategies for all metal producers, as smaller volumes result in lower disposal or reclamation costs. Sulphide also readily forms metal sulphides, the solubilities of which are very low in comparison to the corresponding hydroxides (Kaksonen *et al.*, 2003; Hao, 2000) and carbonates (El Bayoumy *et al.*, 1999), hence even moderate sulphide outputs can effectively precipitate metals, reducing levels to well below those permitted for environmental discharge (White *et al.*, 1997). Additionally, valuable metals can be recovered from the sulphide sludges (Kaksonen *et al.*, 2003).

The cost of chemically produced H_2S is no longer an obstacle to the implementation of sulphide precipitation. The defining line between chemical and biological wastewater treatment becomes blurred as more and more research has focussed on the use of biological sources of sulphide gas. The most commonly studied source of sulphide gas is a group of organisms known as sulphate-reducing prokaryotes (SRP). The SRP include a range of anaerobic, mesophilic bacteria – the sulphate-reducing bacteria (SRB) (White *et al.*, 1997). Sulphate-reducing prokaryotes can be broadly defined as a mixed group of nutritionally and morphologically diverse, strictly anaerobic eubacteria and archaebacteria capable of utilizing oxidised sulphur compounds, including sulphate, as electron acceptors for the oxidation of organic compounds such as organic acids, fatty acids and alcohols, which act as carbon and electron donor sources (Brüser *et al.*, 2000). A significant aspect of SRP metabolism is the production of hydrogen sulphide (H_2S), a strong reducing agent, capable of inhibiting the growth of both anaerobic and aerobic microorganisms (O'Flaherty and Colleran, 2000). Hydrogen sulphide production is via a process known as dissimilatory sulphate reduction, where the sulphate ion is utilized as an oxidant for the degradation of organic matter, i.e. as an electron acceptor for the oxidation of carbon substrates (Equation 1.1).

$$2Lactate + 2SO_4^{2-} \rightarrow 6HCO_3^- + 3HS^- + H^+ \qquad \textbf{[1.1]}$$

Almost all of the sulphate reduced is released as sulphide and may be converted to HS^- or H_2S (Brüser *et al.*, 2000).

A second process, termed assimilatory sulphate reduction, is responsible for the availability of sulphur for incorporation into amino acids (Figure 1.3). Plants, animals and bacteria, without exception, require sulphur for the synthesis of proteins. The highest oxidation state of sulphur, the sulphate ion (SO_4^{2-}) must first be reduced to sulphide (S^{2-}) by bacteria, fungi and plants before it can be incorporated into amino acids. The assimilatory reduction of sulphate is common in prokaryotes, plants and fungi, while the dissimilatory pathway is restricted to eubacteria and archaebacteria only (Brüser *et al.*, 2000). The SRP perform both dissimilatory and assimilatory sulphate reduction and generate sulphide (H_2S/HS^-), with dissimilatory reduction products far exceeding assimilatory reduction products.

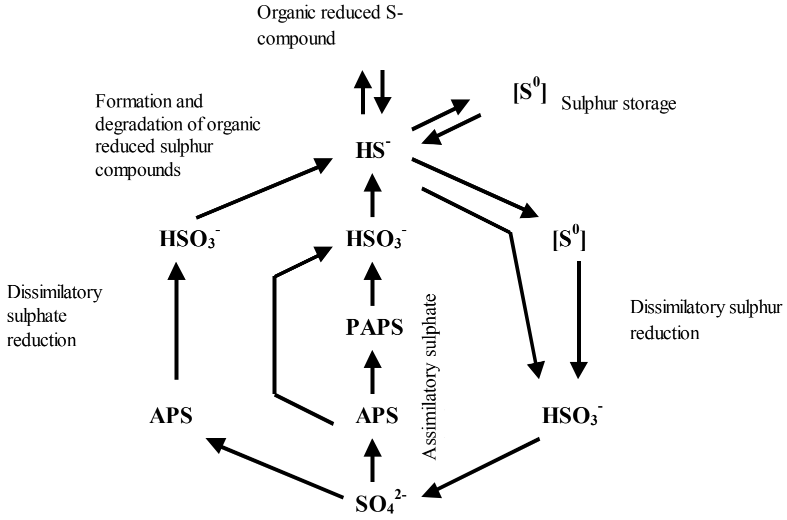


Figure 1.3 The biological sulphur cycle ([S^0]: compound in which 0 oxidation state occurs, such as polythionates, polysulfanes, etc., APS: adenosine-5'-phosphosulphate. PAPS: phosphoadenosine-5'-phosphosulphate) (Brüser *et al.*, 2000).

Currently, 18 genera of dissimilatory SRP are known, and have been placed into two broad groups based on preferences for carbon and energy sources. Group I contains genera such as *Desulfovibrio*, *Desulfomonas*, *Desulfotomaculum* and *Desulfobulbus*. This group can use lactate, pyruvate, ethanol or certain fatty acids as carbon and energy sources. The second group includes genera such as *Desulfobacter*, *Desulfococcus*, *Desulfosarcina* and *Desulfonema* that specialise in the oxidation of fatty acids, particularly acetate (Madigan *et al.*, 2003). In conjunction with a large consortium of other micro-organisms (mainly methanogenic and acetogenic bacteria), SRP are responsible for the complete degradation of organic matter under anaerobic conditions (Figure 1.4).

The habitat of SRP is restricted to anaerobic areas containing high levels of inorganic sulphate and a suitable carbon source, such as waterlogged soils and muds, sewage pipes, drains and pits, stagnant ponds and the rumens of ruminant animals. The anaerobic regions of marine and estuarine sediments are characterized by high sulphate contents and so are primary growth sites for SRP. Carbon sources in this habitat are provided by heterotrophic activities in the water column overlying the sediment, or from a direct organic input, such as sewage. Sulphate-reducing bacterial activity has also been noted in freshwater sediments (Gibson, 1990).

Sulphate reducers have been used successfully to treat electroplating rinse effluent (Song *et al.*, 1998) and copper-laden wastewater (Jalali and Baldwin, 2000). Van Hille *et al.* (1999) reported on the application of SRP in the treatment of AMD, where the SRP were able to significantly reduce sulphate levels and produce enough alkalinity to raise the pH to acceptable levels. This was later supported by Kaksonen *et al.* (2003). This method of AMD treatment has also been used to treat water at a disused mine in France, where the selective precipitation of metals for recovery was also investigated (Foucher *et al*., 2001). The immobilization of a number of other toxic metal ions in sulphide ores such as uranium, thorium and radium has also been shown to be efficient (Groudev *et al*., 2001).

A number of large-scale processes utilize biological sulphate reduction and metal precipitation as significant components of metal removal strategies. Metal sulphide precipitation is especially significant in the operation of both constructed and natural wetland systems (White *et al*., 1997). Studies conducted by Machemer and Wildeman (1992) showed that sulphide precipitation eventually becomes the dominant process for metal removal in constructed wetlands. Machemer *et al.* (1993) reported the same phenomenon during studies conducted at the Big Five Tunnel in Idaho Springs, Colorado.

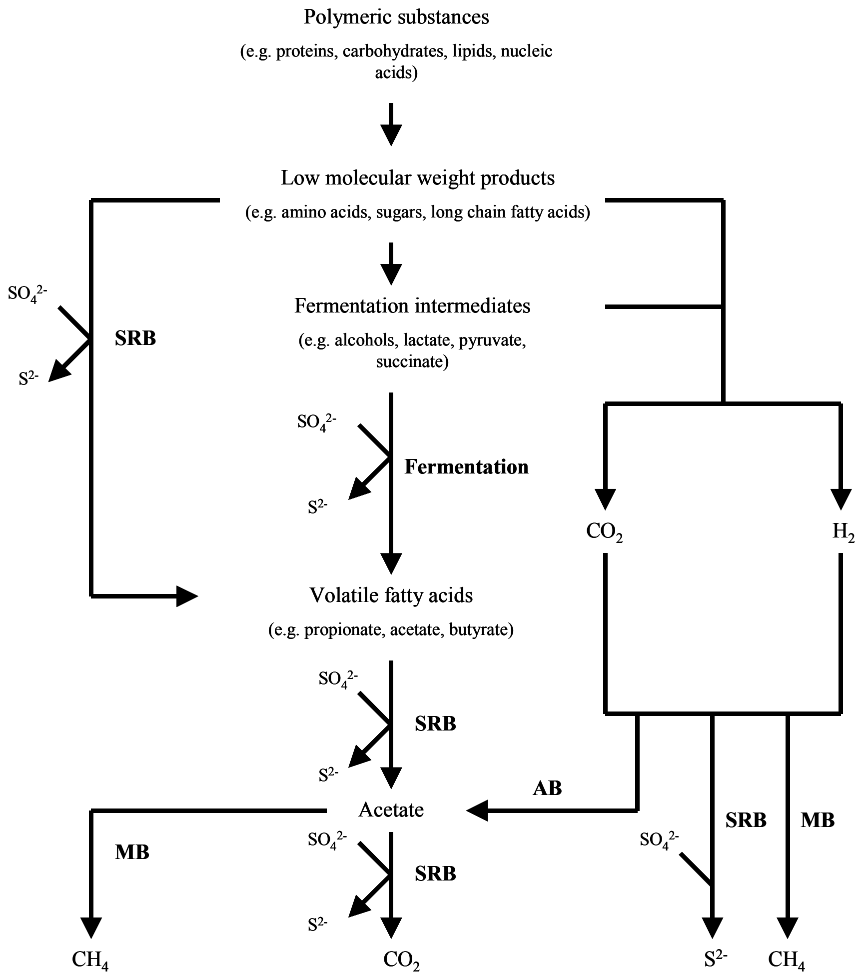


Figure 1.4 Pathway of the anaerobic degradation of organic matter, showing potential interactions of sulphate-reducing bacteria. (*SRB* = sulphate-reducing bacteria; *MB* = methanogenic bacteria; *AB* = acetogenic bacteria) (adapted from Lens *et al.*, 2000).

The possible application of SRP-generated H_2S in the precipitation of metal ions has been studied in a number of intensive process reactor designs. These include upflow anaerobic sludge blanket reactors (UASB) (Weijma *et al.*, 2003; Yamaguchi *et al.*, 2001), anaerobic contact processes, anaerobic filters (Elliott *et al.*, 1998; Dvorak *et al.*, 1992), hybrid reactors (Nedwell and Reynolds, 1996), fluidised-bed reactors (FBR) (Kaksonen *et al.*, 2003) and extractive membrane bioreactors (EMBR) (Chuichulcherm *et al.*, 2001).

1.4.2 MEMBRANE BIOREACTORS

Stephenson *et al*. (2000) define a membrane as a material through which one type of substance can pass more readily than would others. The membrane acts as a semi-permeable barrier, capable of separating one bulk solution phase from another while still allowing transfer (either convective or diffusive) of small molecules present in solution in either direction across the barrier, and preventing the simultaneous transport of another larger molecule (Kentish and Stevens, 2001). When treating wastewater, the membrane may act in a number of ways, and these have produced three distinct membrane bioreactor (MBR) forms.

The biomass separation MBR requires a membrane to reject pollutants and allow purified water to permeate the membrane. Since the 1980s solid-separation MBR technology has been successfully applied to a range of industrial wastes, including oily wastes (Knoblock *et al*., 1994), food wastes (Mallon *et al*., 1999), tannery effluents (Yamamoto and Win, 1991) and landfill leachates (Mishra *et al*., 1996). In Tunisia, wastewaters from the detergent and cosmetic industries are being targeted for MBR treatment. The Tunisian standard level for discharge of wastewater containing surfactants is 5 mg/L. However, the industries are producing up to 100 000 t of wastewater a year containing more than 1 g/L of surfactants. This type of MBR system has been shown to eliminate between 0.065 to 0.15 g/L/h of surfactant with a hydraulic retention time of 5 h (Dhouib *et al*., 2003).

The membrane aeration bioreactor (MABR) makes use of membranes in order to transfer gas (e.g. oxygen) into wastewater where it is required to augment microbial degradation (Casey *et al*., 1999). The need for increased oxygen mass transfer into wastewaters in cases where the oxygen requirements for degradation of the pollutant were too high for conventional aeration processes prompted the development of the membrane aeration bioreactor concept. This membrane bioreactor concept may also be applied when the possibility exists that the bubbling of air would result in either the stripping of volatile organic carbons or of foaming of industrial wastewaters (Pankhania *et al*., 1999). The membrane itself may play a dual role in the reactor, namely as a means for supplying oxygen and by providing a substrate for supporting biofilm formation. Membrane aeration bioreactors have been used to treat a wide variety of wastewater types and have been shown to be particularly effective in treating high oxygen demanding wastewaters (Yamagiwa and Ohkawa, 1994). They have also been applied to the biodegradation of volatile organic compounds (Kniebusch *et al*., 1990), combined nitrification (Timberlake *et al*., 1988), denitrification and/or organic carbon degradation in a single biofilm (Hirasa *et al*., 1991).

In the extractive membrane bioreactor (EMBR), the membrane acts to extract pollutants from a wastewater (Livingston, 1994). The concept of an extractive membrane bioreactor is shown in Figure 1.5. A selectively permeable membrane is used to separate an industrial wastewater containing the organic compound to be degraded, from a microbial culture maintained in an aqueous biomedium at the other surface. The pH and ionic strength of the wastewater cannot influence the makeup of the biomedium in any way, as the membrane is effectively impermeable to any inorganic or charged species in the wastewater. This allows for the controlled maintenance of the biomedium conditions to provide optimal growth conditions for the microbial culture in spite of the biologically hostile makeup of the wastewater (Livingston *et al*., 1998).

Wastewaters arising from metal industries usually contain compounds that may be toxic or inhibit the growth of microorganisms. They are also often saline or exhibit extremes of pH. This description fits that of a wastewater suitable for treatment via EMBR. However, if the purpose of the treatment of these wastewaters is to extract or recover the metal ions, a specialized EMBR system has been devised incorporating the use of biological H_2S as a precipitating agent (Chuichulcherm *et al*., 2001). The use of biologically produced H_2S is already considered a conventional method of precipitating metals from wastewaters. In the conventional method the SRP are either grown in direct contact with the wastewater and the resulting H_2S causes metal precipitation, or the gas is collected from a bioreactor and sparged through a wastewater, resulting in precipitation. These metal sulphides are insoluble and can thus be easily separated. However, these applications are limited by the inhibition of microbial activity due to the biologically hostile characteristics of the wastewater and/or the space requirements for a bioreactor and gas extraction unit. An EMBR system can be used to solve these limitations by preventing the direct contact between the SRB and the wastewater.

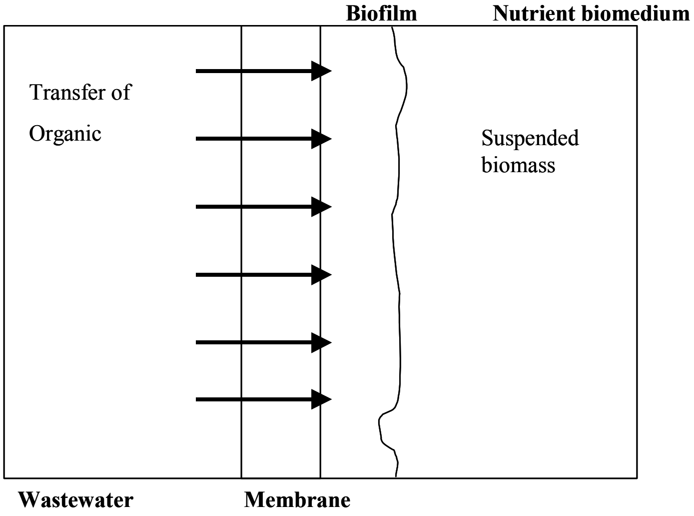


Figure 1.5 Schematic diagram of the EMBR process. Organic pollutants selectively diffuse through the membrane material into the biomedium phase where they are biodegraded in the biofilm (Stephenson *et al*., 2000).

1.5 NUCLEATED PRECIPITATION OF METAL IONS

A major disadvantage of conventional continuous-flow chemical precipitation processes is that they generally require a number of steps, each requiring a separate tank environment. Added to the space disadvantage of needing separate reaction and settling tanks, dewatering and/or solidification is often necessary before disposal can be effected.

Recent research at the Hong Kong University of Science and Technology has resulted in the development of a single-step space-saving precipitation process for the removal of heavy metals by chemical precipitation (Sun and Huang, 2002). The new method, known as 'nucleated precipitation' or 'pellet crystallization' allows for soluble metal ions to become coated or plated onto sand particles present in a fluidized sand bed and is based on the design results of similar systems, discussed below.

Nielsen *et al*. (1997), at a Danish company called Krüger A/S, developed Krüger's fluid-bed technique and tested it as a means for removal of heavy metals from high ionic strength wastewaters. The process is operated by continuous addition of manganous or ferrous ions and an oxidising agent, e.g. O_2, H_2O_2, $KMnO_4$, to the wastewater. Both addition and mixing take place in the fluidized bed reactor (FBR), which contains the carrier material. By carefully controlling the process conditions, the oxidation of manganous/ferrous ions can be engineered to take place heterogeneously after adsorption to the carrier material. The surface of the carrier material is coated with an adsorptive granulate layer of either ferric oxyhydroxide or manganese dioxide, and dissolved metal species will co-precipitate or adsorb to the granulate and will be built into the constantly increasing granulate layer. At optimal operation, the fluidized bed reduced the dissolved metal loadings by 99 % (nickel), 92 % (cadmium) and 97 % (zinc). The granulate waste product exhibits excellent handling properties; the density of the granulate waste is 2 – 3 kg/L and the coating has a very low water content of between 10 and 20 %.

This system has also been shown to remove in excess of 99 % of chromate ions present in a spiked tap water sample by catalysing the redox reaction between the ferrous oxyhydroxide ion and chromate (Aktor, 1994). In a later study, also focussed on chromium, Sun and Huang (2002) found that while using nucleated precipitation technology to treat plating wastewater, half of the hexavalent chromium present in the wastewater was co-precipitated with copper, nickel and zinc. But, due to the inability of chromium(VI) to form precipitates with either hydroxide or carbonate, this removal was attributed to two mechanisms, i.e. co-precipitation as $CuCrO_4$ crystals and adsorption. Wilms *et al.* (1992) dosed a carbonate precipitation reagent into a reactor to remove silver through the crystallization of silver carbonates on the surface of sand grains. The seeding sand could be reused after the pellets were dissolved in acid, as the carbonate escapes as CO_2, and a concentrated metal solution is obtained. They found that this process was applicable to almost all heavy metals, but depending on the metal, the optimal process conditions could be very different.

Fluidized-bed reactor processes have been used in a wide range of water and wastewater treatment plants. Harms and Robinson (1992) applied the process as a drinking water softener, where $CaCO_3$ was crystallized. Chou and Huang (1999) also made use of the supported FeOOH in an FBR and catalysed the oxidation of benzoic acid. The removal of phosphate from wastewater using calcium phosphate crystallization has also been studied (Seckler *et al.*, 1996)

In the system to be investigated for application to rhodium recovery, sodium carbonate is added to the fluidized bed to induce nucleated precipitation onto the sand particles. Copper, nickel and zinc were used as model metals for removal and the system achieved greater than 95 % removal for all three metals (Zhou *et al*., 1999). Lee *et al*. (2004) made use of a very similar setup for the removal of copper. Similar to Zhou *et al*. (1999) they found that the optimum molar ratio of carbonate/metal for nucleated precipitation was 2. Their results indicated that, with good mixing of the carbonate and metal solutions in the presence of the sand grains, 96 % copper removal efficiency could be achieved when the influent copper concentration was 10 mg/L. Parameters such as pH, adsorbent concentration, competing adsorbates and complexing ligands all affect the adsorption and/or co-precipitation of metal ions. In particular, controlling pH can increase the efficiency of these processes significantly. In theory, a decrease in pH increases anion removal but decreases cation removal (Nielsen *et al*., 1997).

A further parameter of importance is the molar ratio of carbonate ions to metal ions. When the carbonate solution is added to the reactor, two precipitation reactions take place, nucleated precipitation and discrete precipitation (Figure 1.6). Nucleation allows the precipitate to become coated on the sand surface, while discrete precipitation takes place in the bulk solution. When the molar ratios are too low, precipitation does not take place, but when the ratios are too high, precipitation is greatly accelerated and most metal ions will precipitate in the bulk solution before being coated on the sand particles (Zhou *et al*., 1999). Or, put another way, the essential condition for heavy metal removal in this type of process is supersaturation of the reactant solution. This supersaturation drives the crystallization onto the media in the FBR. When supersaturation occurs, nucleation occurs immediately, but the supersaturation levels must not be so high as to initiate discrete precipitation (Lee *et al*., 2004). Wilms *et al*. (1992) further reiterate this and go on to state that the mixture must become supersaturated with respect to the solubility of metal carbonate, but not with respect to metal hydroxide, as metal hydroxides are not crystalline and form a voluminous water-rich sludge. In all cases, discrete precipitation cannot be classed as recovery of the metal, as the precipitate will pass out of the reactor and will not be available for further reuse.

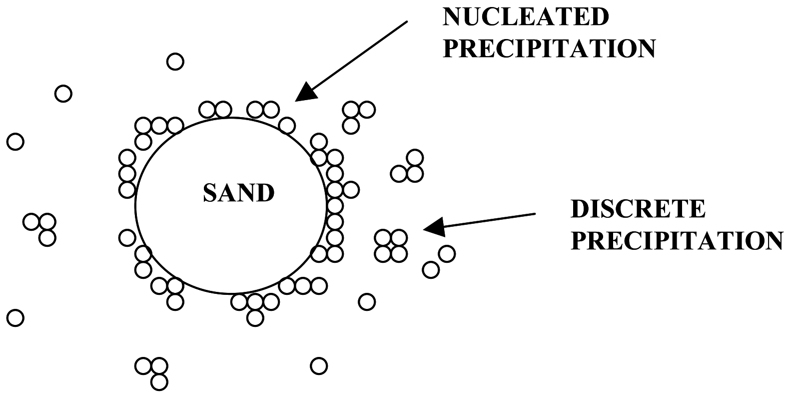


Figure 1.6 Schematic representation of nucleated and discrete precipitation (Zhou *et al.*, 1999).

1.6 BIOSORPTION OF METAL IONS FROM AQUEOUS SOLUTION

The terms biosorption and bioaccumulation are often used interchangeably to describe the retention of metal ions from aqueous solutions by a wide variety of biomass types. Whether or not this interchangeable use of the terms is valid, depends on the state of the biomass, i.e. only living biomass may bioaccumulate metal ions, while both living and dead biomass may biosorb metal ions. Vegliò and Beolchini (1997) categorised the metal retention mechanisms according to both the dependence on the cell metabolism and to the location of the retained metal on/in the cell. Figure 1.7 shows the mechanisms categorized according to their dependence on the cellular metabolism of the biomass.

Thus, biosorption is the term used to describe a number of passive modes of metal uptake by biomass. As it is a passive process, the biomass need not be living, and in fact, a number of highly efficient commercial biosorbents are dead. Sequestration of metal ions by different parts of the cell wall can occur via a number of diverse paths. These include complexation, adsorption, ion exchange, coordination, chelation, and inorganic microprecipitation (Vegliò and Beolchini, 1997; Volesky, 1990).

Bioaccumulation, on the other hand, is an active mode of metal sequestration, reliant on the metabolic activity of the cell. A major disadvantage of this process is that the presence of these metal ions within the cell can greatly inhibit that activity. A number of theories have been proposed as to why a cell would become tolerant to non-trace metal ions within the cell. These include a reflection of the ability to survive in environments with high concentrations of metals or to retain high concentrations of metal without dying (Malik, 2004).

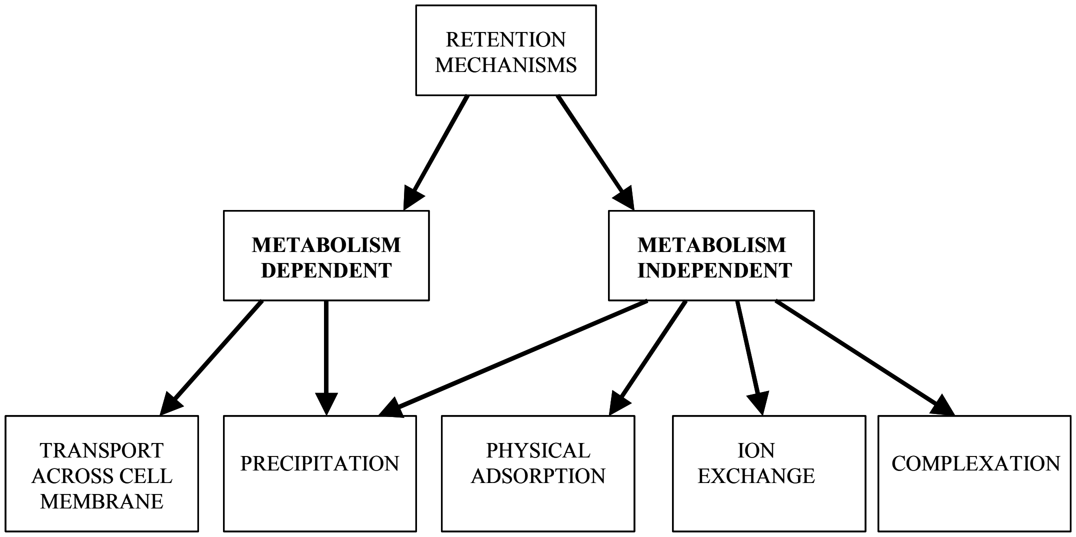


Figure 1.7 Metal retention mechanisms categorized according to whether or not the mechanism is reliant on metabolism (adapted from Vegliò and Beolchini, 1997).

Biosorption is a process that makes use of inexpensive, non-living biomass to remove toxic heavy and precious metals from industrial effluents or, as defined by Dönmez *et al.* (1999), "the accumulation and concentration of pollutants from aqueous solutions by the use of biological materials, thus allowing the recovery and/or environmentally acceptable disposal of the pollutant." Biosorbents are prepared from naturally abundant or waste biomass such as algae, fungi, plants or bacteria that have been killed either in a production process or as a pre-treatment step in their use as a biosorbent.

The advantages of this process over conventional processes for metal removal such as lime precipitation, ion exchange and biogenic sulphide production include low operating costs, sludge disposal minimization, high efficiency when challenged with dilute effluents and no nutrient requirements (Kratochvil and Volesky, 1998). The efficiency of the process is governed by factors which include the type of metal, the ionic form of the metal in solution and on the binding site on the biomass responsible for uptake of the particular metal (Volesky, 1990).

These advantages have resulted in vast amounts of research in this field and a number of commercializations. However, of all of these commercial ventures into biosorption for wastewater treatment and metal value recovery, none has been successfully integrated into industrial use (Kratochvil and Volesky, 1998; Tsezos, 2001). The most important physical characteristics of a successful biosorbent are hardness, porosity, particle size, and density. These characteristics ensure that the biosorbent is capable of withstanding high liquid pressures that may be experienced in the biosorption environment and still maintain superior removal efficiency. A broad tolerance to a number of factors including temperature, pH, and solvent content are also highly beneficial, especially in cases where the effluent to be treated is highly acidic in nature or contains organic compounds that could possibly render the biosorbent useless. Potential for the regeneration and reuse of the biosorbent is also important. This is usually much easier to accomplish when using non-viable biomass, as regeneration usually entails elution with mineral acids (Wilhelmi and Duncan, 1996) or toxic complexing and chelating ligands such as thiourea (Godlewska-Żyłkiewicz, 2003) or thiocyanates.

The availability of a specific biomass is also a major factor in the final choice. An enormous pool of possible biosorbent material exists in nature and many of these natural biosorbents are cheaply available as they can often be acquired as spent biomass from pre-existing processes, such as spent yeast from breweries or bacterial biomass from pharmaceutical industries. The use of waste biomass is currently in favour as it provides an environmentally positive and sustainable disposal and reuse cycle (Wase *et al.*, 1997). Natural biosorbents such as peat, weed plant biomass and agricultural wastes are also widely available.

The cell wall composition of the biomass chosen also plays an important role in the efficiency of the process. The quantity and type of the active sites on the cells may be a major factor in the binding behaviour of the metal ion of interest. These differences were found to result in the differing affinity shown by a biomass to a range of metals. For example, *Datura innoxa* shows a higher affinity for gold than for copper and aluminium and Sphagnum moss shows a higher affinity for copper than for gold and mercury (Lujan *et al.*, 1994).

The complexity of the cell surface implies that there are many possible explanations for how metal ions are sequestered by the cell. In the case of non-viable biomass, these interactions are generally physicochemical processes such as physical adsorption, ion exchange, and microprecipitation (Pagnanelli *et al.*, 2000). These interactions occur between structures on the cell walls such as carboxylate, phosphate, sulphydryl, amino, amide and hydroxyl groups (Esposito *et al.*, 2002; Vasudevan *et al.*, 2002).

In a review of metal sorption by fungi, Kapoor and Viraraghavan (1995) suggest that adsorption of metal is achieved via two mechanisms. The first is uptake regulated by the functional groups listed above and the second is through physico-chemical interactions based on adsorption phenomena. In some cases, e.g. uptake of radionuclides, both processes are involved, while for most other heavy metals, the first plays a more important role.

A review of bacterial sorption (Urrutia, 1997) supports this suggestion, postulating that metal sorption occurs in two stages. The first stage is one of mainly electrostatic interaction and is termed the ‘adsorption’ phase. In the second stage, these electrostatically adsorbed ions nucleate the deposition of more metal ions and a precipitate forms at the cell surface.

Physical Adsorption/Ion Exchange

The basis for physical adsorption is the presence of van der Waals’ forces between the cell surface and the metal ion of interest. Electrostatic interactions have been implicated in copper biosorption by the bacterium *Zooglea ramigera* and the alga *Chlorella vulgaris* (Aksu *et al.*, 1992). Ion exchange interactions are characterized by a stoichiometric exchange of metal ions for protons and/or other metal ions at relevantly charged cell wall components (Schneider *et al.*, 2001).

Microprecipitation

The precipitation or condensation of metal hydroxides onto biological surfaces occurs when, despite there being a metal ion concentration, in the bulk liquid, far lower than the solubility limit, that limit is exceeded at the surface. This accumulation will occur if a net negative charge exists within that microenvironment (Schneider *et al*., 2001).

All three mechanisms contribute to metal biosorption. The model described by Dzombak and Morel (1990) attempts to illustrate the relative contributions each make. Figure 1.8 is a representation of this model, taken from Schneider *et al*. (2001) in which the sorption of copper(II) is shown.

However simple the processes involved may seem, the actual mechanisms used are thought to vary depending on the biosorbent used and/or the metal to be sorbed. Two examples of this were discovered early on in the development of the knowledge of biosorption mechanisms. Tsezos and Volesky (1982a; 1982b) proposed two different processes to describe the sorption of uranium and thorium by non-living *Rhizopus arrhizus* cells based on experimental results. In the case of uranium, they suggested an initial complex formation step, a metal nucleation step and a final complex hydrolysis and surface precipitation step. With thorium metal, the results suggested the initial coordination/complexation step followed by hydrolysis and adsorption to the cell wall.

Bacterial biosorption is by far the best studied. This is due to a number of factors that make bacterial biomass a very attractive option for the removal of heavy metals. These include their small size, their high specific surface area, their widespread availability, their ability to grow under strict conditions and their wide range of environmental tolerances. Studies of both Gram-positive and Gram-negative bacterial cell walls have shown that Gram-positive walls bind up to 10 times more metal than Gram-negative walls. This is due to their simple peptidoglycan structure and the anionic carboxyl and phosphoryl groups contained in the polymers of the cell wall (Urrutia, 1997).

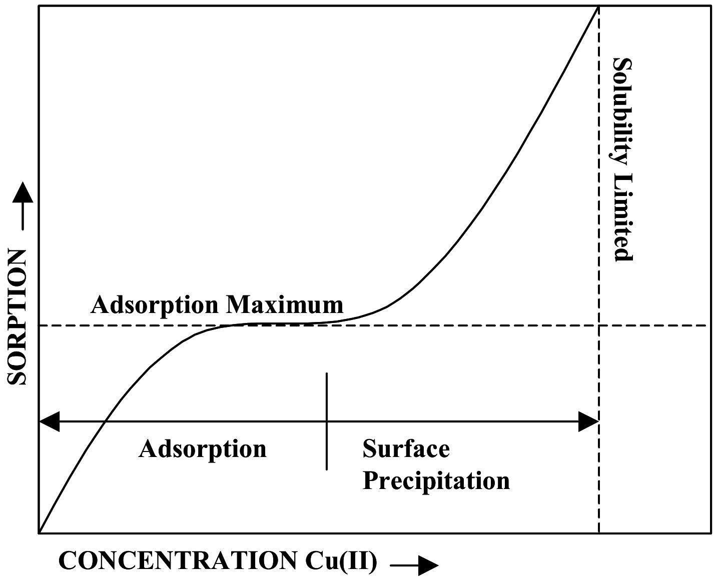


Figure 1.8 A representation of the Dzombak and Morel (1990) model illustrating the relative contributions of adsorption and surface precipitation to metal sorption (Schneider *et al.*, 2001).

Selatnia *et al.* (2004) investigated the use of granulated and NaOH-pretreated *Streptomyces rimosus* biomass as a lead(II) biosorbent. They found that the sodium ions exchanged far more easily with the lead ions that a purely protonated biomass did and achieved a maximum uptake of 135 mg Pb^{2+}/g. The photosynthetic bacteria *Rhodobacter sphaeroides* S and a *Rhodovulum* species were tested for their ability to remove copper ions from seawater. Both species achieved greater than 90 % removal over a 7-day experiment. However, no attempt was made to distinguish biosorption from accumulation in this case, as the bacteria were actively respiring (Watanabe *et al.*, 2003). Zouboulis *et al.* (2004) isolated two bacterial strains from metal-polluted soils that showed a high affinity for cadmium and hexavalent chromium. *Bacillus laterosporus* and *Bacillus licheniformis* achieved maximum uptakes of 142.7 mg/g and 159.5 mg/g of cadmium, respectively and between 60 and 75 mg/g of chromium.

Fungi and yeast species are of significant interest as biosorbents due to their abundance as waste from fermentation processes and their relative ease of cultivation and as such, they are a ready source of cheap biomass. However, the small particle size and low strength of fungal cells can cause difficulties in biosorption processes, so fungal biosorption applications are preferred only if the biomass is immobilized or pelletized before use (Kapoor and Viraraghavan, 1995).

In two separate studies, Arica *et al.* (2003; 2004) immobilized *Funalia trogii* and *Phanerochaete chrysosporium* in calcium-alginate beads. The *Funalia trogii* beads removed 403.2 mg Hg/g, 191.6 mg Cd/g and 54 mg Zn/g, while the *Phanerochaete chrysosporium* removed 395 mg Pb/g and 52 mg Zn/g. Yan and Viraraghavan (2003) used *Mucor rouxii* to remove lead, cadmium, nickel and zinc and found that the fungus showed good capacity for biosorption in bi- or multimetal systems.

Comparative studies of immobilized *Saccharomyces cerevisiae*, viable and non-viable, showed that the non-viable biomass adsorbed copper faster than viable biomass (Huang *et al.,* 1990). Brady and Duncan (1994) found that viable immobilized *S. cerevisiae* completely removed copper, cobalt and cadmium from aqueous solutions, suggesting that yeast biomass would serve as an effective bioaccumulator for the removal and/or recovery of metals. It was also found that bound metal(s) could be removed from the biomass by using ethylenediamine tetraacetic acid (EDTA). This means that the biomass can be recycled with very little loss in accumulation capacity. Vasudevan *et al.* (2003), while investigating the biosorption of cadmium to Baker's yeast, found that the amount of metal adsorbed at equilibrium is proportional to the initial metal concentration divided by the sorbent mass used. They also found that the maximum cadmium uptake by Baker's yeast was 91.7 mg/g.

Algal biosorption capacity is generally attributed to characteristics of the cell wall such as the fibre-like structure and the amorphous embedding matrix of polysaccharides. These polysaccharides include alginates and sulphated polysaccharides such as fucoidan, which are known to have high affinities for divalent and trivalent cations, respectively. Alginates are found within the cell wall and as components of the intercellular substance and comprise up to 40 % (dry matter) of the cell wall (Sheng *et al*., 2004). Of the four algal species Sheng *et al*. (2004) investigated, *Sargassum* sp. and *Padina* sp. showed the most potential as biosorbents for metals such as lead, copper, cadmium, zinc and nickel. *Ulothrix zonata* exhibited a maximum uptake of 176.2 mg Cu/g when tested by Nuhoglu *et al*. (2002). They suggested that the high value implies strong adsorption via electrostatic interactions. Tien (2002) compared the adsorptive capacities of four algae, *Oscillatoria limnetica*, *Anabaena spiroides*, *Eudorina elegans* and *Chlorella vulgaris*. Each showed significantly different sorption activities when challenged with copper, cadmium and lead due to the different cell surface characteristics, resulting in multiple functional binding sites. The author suggests that this selectivity would be useful for the treatment of a wide variety of industrial effluents.

Higher plants provide a wide range of biosorbent materials. Viable aquatic plant biomass has been investigated for the decontamination of wastewater via wetland schemes (de Wet *et al.*, 1990), and the use of pond systems. Promising biosorbents include duckweed (*Lemna minor*) and the water hyacinth (*Eichornia crassipes*) (Volesky, 1990). *Ceratophyllum demersum*, also an aquatic plant, was found to rapidly bind lead, zinc and copper, reaching equilibrium within 20 minutes. Maximum metal uptake levels of 6.17 mg Cu/g, 13.98 mg Zn/g and 44.8 mg Pb/g were recorded (Keskinkan *et al.*, 2004). Al-Subu (2002) compared the removal efficiencies of three tree species with respect to lead. The decaying leaves of cypress (*Cupressus sempervirens*), cinchona (*Eucalyptus longifolia*) and pine (*Pinus halepensis*) showed varying affinities according to the following affinity series: pine>cypress>cinchona. de Carvalho *et al.* (2003) went a step further and compared the affinity of dried leaves of *Maitenus truncato* for copper with the separated fibres of the same leaves. The fibres showed much higher sorption efficiency, possibly due to the larger surface area available for adsorption.

Major constituents of fungal cell walls include chitin and chitosan. They are both natural polysaccharides and are found widely, not only in fungi, but also in animals such as crustaceans and insects. The major commercial sources, however, are the exoskeletons of crabs obtained as waste from seafood processing (Niu and Volesky, 2003). Both of these compounds have been found capable of metal ion uptake. Chitin is a polymer of N-acetyl-D-glucosamine. Chitosan is a completely deacetylated derivative. Uptake of metals such as iron, zinc, copper, lead, mercury and uranium by chitin is varied due to changes in the chitin and chitosan contents of the cell wall changing during growth (Kapoor and Viraraghavan, 1995). Metal uptake by chitin and chitosan is pH dependent, with optima between pH 3 and pH 4. It is suggested that the uptake mechanism is a combination of ion exchange and complexation with chitin nitrogen atoms (Kapoor and Viraraghavan, 1995; Volesky, 1990). Kartal and Imamura (2004) used a combination of chitin and chitosan to remove copper, chromium and arsenic from waste sawdust treated with chromated copper arsenate and achieved 74 % copper, 62 % chromium and 63 % arsenic removal. Niu and Volesky (1995) used waste crab shells to recover anionic metal species such as gold-cyanide, selenate, chromate and vanadate from aqueous solutions, and found that they could not conclusively determine the functional groups responsible for sorption, but suggested it may be amine or amide groups present on the cell walls.

A rapidly growing number of waste products have been screened for biosorptive abilities, as they have been recognized as being the most cost effective solutions to commercialization of biosorption processes. Agricultural wastes such as carrot residues (Nasernejad *et al*., 2004), crab shells (Vijayaraghavan *et al*., 2004), olive mill residues (Vegliò *et al*., 2003), rice milling by-products (Tarley and Arruda, 2004), rice bran (Wang and Qin, 2004) and wheat husks (Basci *et al*., 2004) have been screened for biosorptive activity. Metals such as copper, zinc, chromium, cadmium, nickel, aluminium and lead have been shown to adsorb to some or all of these. In all cases, encouraging potential for efficient removal of metal ions from aqueous solutions was shown. Table 1.2 summarizes a small number of biosorbents that have been investigated in 'real wastewater' situations.

Table 1.2 Examples of biosorbents tested in metal-bearing wastewaters.

Biosorbent	Target metal waste	Target metal	Success	Reference
Activated sludge	Electroplating wastewater	Zn, Cu, Cd, Ni, Cr and Cr	96% Zn within 15 minutes	Atkinson *et al*., 1996
Hen eggshell membrane	Electroplating wastewater	Au(III)	618 mgAu/g biosorbent	Ishikawa *et al*., 2002
Grape stalks/ cork powder	Acid mining wastewater	Fe	8g/L removed 85% Fe	Santos *et al*., 2004
Staphylococcus sp.	Copper chemical mechanical planarization wastewater	Cu	>90% Cu removed	Stanley and Ogden, 2003

1.7 CONCLUDING REMARKS

The three technologies discussed are all novel alternatives to conventional metal recovery strategies, and in particular PGM recovery. Biosorption and sulphide precipitation are both well-researched areas and much data exists regarding their efficiency with regard to heavy metal removal from solution. However, there is a paucity of data involving the biosorption of precious metals, especially PGMs and no data exists regarding the application of the EMBR-SRP system to any metal other than zinc. There is also no data showing the efficiency of nucleated precipitation applications in recovering precious metals. In spite of this lack of data to prove or disprove the efficiencies of these technologies when challenged with PGMs, each was chosen, based on novelty, as possible methods for the recovery of rhodium from a precious metal refinery wastewater.

Each technology will be broadly screened to determine whether further investigation would result in a viable rhodium recovery process, and depending on these initial results, detailed optimisation of the relevant technology will be undertaken at a later stage.

CHAPTER 2

PLATINUM GROUP METALS IN WASTEWATERS

2.1 MINING AND REFINING OF PLATINUM GROUP METALS

Platinum group metals (PGMs) or elements (PGEs) are collective names used when referring to the six precious metal elements – platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), rhuthenium (Ru) and osmium (Os). The average concentration of these metals in the earth's crust is estimated to be in the range of 0.001 - 0.005 mg/kg for Pt, 0.015 mg/kg for Pd, 0.0001 mg/kg for Rh, 0.0001 mg/kg for Ru, 0.005 mg/kg for Os and 0.001 mg/kg for Ir (Ravindra *et al*., 2004). For centuries, these precious metals have been sought after in the form of jewellery and ornaments. As scientists uncovered the physical and chemical properties of these metals, their application expanded to many other fields. The PGMs have unique properties of corrosion resistance, heat resistance, high melting point, high mechanical strength, good ductility and catalytic activity (Ravindra *et al*., 2004). These properties have lead to their use in fields such as electronics, the glass, electrical, petroleum, and medical industries and as dental alloys and automotive catalysts (Ravindra *et al*., 2004; Johnson-Matthey, 2002). Among the PGMs, rhodium has unique catalytic activity. Rhodium is able to reduce nitrogen oxides (NOx) to N_2, and is currently an essential element in the production of automotive catalysts. It is also the most stable of the PGMs, and therefore it is the most difficult to dissolve in aqueous solutions (Kayanuma *et al*., 2004).

All the PGMs are generally associated with each other in the earth's crust. Rhodium therefore occurs wherever the other PGMs are found. However, the relative proportions of the individual metals are not constant for all PGM deposits. Platinum group metals occur naturally in nickel, copper and iron sulphide seams (Ravindra *et al*., 2004). Two of the most important sources of rhodium are the nickel-copper-sulphide ores found in South Africa and Canada, which contain approximately 0.1 % rhodium (Greenwood and Earnshaw, 1989).

The Bushveld Igneous Complex (BIC), formed around 2000 million years ago is the worlds' single largest PGM resource. It consists of a series of distinct layers, three of which are of economic importance as sources of PGMs. These are the Merensky Reef, the Upper Group 2 (UG2) Reef and the Platreef. The Merensky Reef has been the principal source of PGMs since it was first worked in 1925 and now produces 50 % of all the platinum-bearing ore processed in South Africa. The UG2 Reef, in 1999, produced 42 % and the Platreef only began to be exploited on a large scale in 1993 (Johnson-Matthey, 2003). Mill head grades of BIC ore (a measure of the ore's PGM content on entering the first processing stage) are typically between 4 and 7 g/ton. This translates to between 7 and 12 tons of ore being processed to produce a single ounce (28.35 g) of platinum (Johnson-Matthey, 2003). Figure 2.1 shows an overview of the entire process involved in producing that single ounce of platinum.

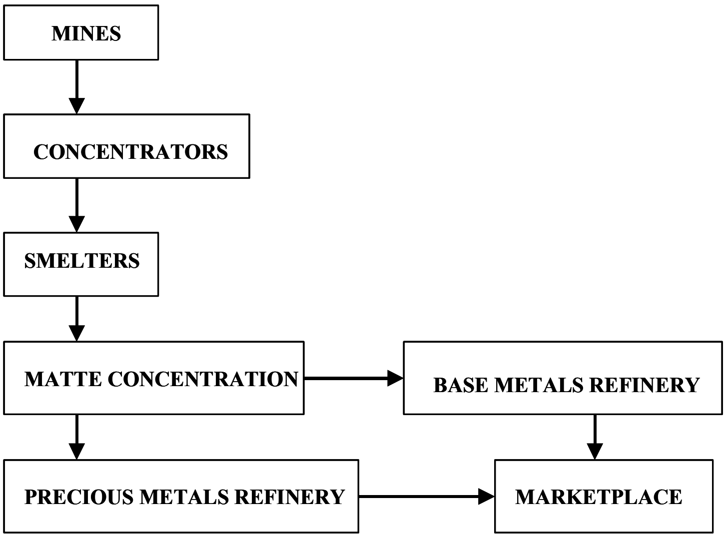


Figure 2.1 Overview of the PGM production process: from mine to marketplace (Robinson, 2002).

In the concentrators, the ore is crushed and milled to reduce rock sizes and expose the minerals containing the PGMs. The rock is mixed with water and other reagents and air is pumped through the mixture to create bubbles to which the PGM-containing particles adhere. These float to the surface and are removed as a soapy froth called concentrate. This process is known as flotation.

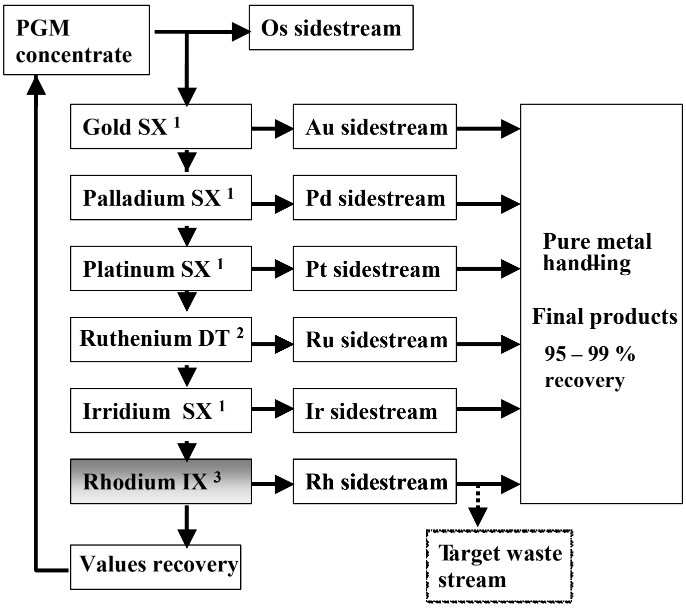


Figure 2.2 Overview of Anglo Platinum Precious Metal Refinery (PMR) flow sheet indicating the wastewater stream targeted in this study. [1] Solvent extraction [2] Distillation [3] Ion exchange (Robinson, 2002).

The PGM concentration of this concentrate varies between 100 and 1000 g/ton (Johnson-Matthey, 2003). The concentrate is dried and smelted in furnaces reaching temperatures of 1500 °C and higher. During this process a matte containing the PGMs is separated from the unwanted minerals, which form a slag and are discarded. The matte is transferred to converters, where air is blown through it in order to remove iron and sulphur. The PGM content of "converter matte" is in excess of 1400 g/ton (Johnson-Matthey, 2003). The next step is to separate base metals from the PGMs. The base metals are transferred to a base metal refinery, where sulphate and metals such as cobalt, nickel and copper are refined for the marketplace. The final stage is the separation and purification of the six PGMs, plus gold, which is a byproduct of the ore body. Figure 2.2 illustrates the methods used and the order in which the metals are extracted from the matte. The soluble metals, gold, palladium and platinum are generally removed first. The insoluble metals are then removed, with rhodium usually last out (Robinson, 2002).

The refined PGMs usually have a purity of over 99.95 % and are produced in a number of forms, including ingots, grains or fine powders known as sponges. However, a relatively large percentage of PGMs are not recovered by the conventional techniques and are stored as wastewater in slime dams (Els *et al.*, 1997).

The complex nature of the solution chemistry of PGMs contributes to the difficulty in developing methods for the separation of these metals from each other (Lloyd *et al.*, 1998; Al-Bazi and Chow, 1984). Precipitation is not readily applicable for selective separation and electrochemical techniques are feasible, but the recovery of the thin metal film deposits from the electrodes may limit its industrial adoption (Lloyd *et al.*, 1998). The current general trend in metal recovery of PGMs from heterogeneous solutions are ion exchange and solvent extraction, often in combination, as the high concentrating efficiency and ease of phase separation advantages of ion exchange cover the inherent disadvantages of solvent extraction, i.e. a lower ability to concentrate metal ions, and phase separation difficulties during multiple and back-extraction phases (Cortina *et al.*, 1998).

When using ion exchange to separate the chloro-complexes of PGMs, it is important to note that the interaction between ion-exchanger and metal ion depends on the charge of the complex. Doubly charged complexes such as $PdCl_4^{2-}$, $PtCl_4^{2-,}$ $PtCl_6^{2-}$, $IrCl_6^{2-}$, $RuCl_6^{2-}$ and $OsCl_6^{2-}$ are strongly sorbed, whereas triple-charged complexes such as $IrCl_6^{3-}$, $RhCl_6^{3-}$, and $RuCl63^-$ are only weakly bound. The sorption efficiency of Rh and Ru also depends strongly on the age of the solution, as the older the solution, the higher the level of aquation and hence the less extractable the species. However, using the difference in electrostatic interaction strength, Rh can be separated from Pt and Pd on an anion-exchanger (Al-Bazi and Chow, 1984). Extraction of PGM chloro-complexes with solvent extraction is simpler for most of the PGMs. Pt and Pd chloro-complexes are inert to aquation, and a highly extractable into organic solvents. Rh, however, is only poorly extracted due again, to its labile character towards aquation, i.e. formation of non-extractable $[RhCl_{6-x}(H_2O)_x]^{x-3}$, ($x = 1$ to 6). A similar phenomenon occurs with Ru. Both Rh and Ir chloro-complexes react very slowly at room temperature to form extractable anionic or neutral complexes. Heating or the addition of a catalyst before extraction accelerates the formation of these extractable species, making them more available for extraction via ion exchange and solvent extraction (Al-Bazi and Chow, 1984)

Conventional ion exchange is often not sufficiently selective to remove single metals from a multi-metal solution (Cortina *et al.*, 1998), e.g. common anion exchangers cannot adsorb negatively charged PGM chloro-complexes selectively, and some complexes are adsorbed too strongly to be eluted efficiently (Lee and Tölg, 1993). Metal-selective resins are being developed that consist of metal-selective functional groups immobilized onto polymeric matrices via chemical bonding or physical adsorption. These resins are known as solvent impregnated resins (SIR). Physical adsorption SIR technology is attractive, as it combines features of ion exchange and solvent extraction, resulting in advantages such as high selectivity, ease of preparation and wide choice of reagents of desired selectivity. The technology is currently being tested as an alternative for use in recovery of PGMs from automotive catalysts. There are two conventional hydrometallurgical recovery methods; oxidative acidic dissolution with aqua regia, and dry chlorination of catalysts to yield a PGM concentrate. Both are complex chemical systems with high reagent consumption, result in severe corrosion, and produce large volumes of toxic liquid waste. When using the SIR technology, PGM leachates are produced as metal-cyanide complexes in high pH aqueous solutions (up to 12.5). The resin has proved capable of selectively recovering Pt from a mixed solution of Pt and Rh. This was found to be caused by the relative need for hydration by the Rh- and Pt-cyanide complexes. The $Rh(CN)_6^{3-}$ complex exhibits a relatively high charge density (3 electric charges carried by 13 atoms) compared to the $Pt(CN)_4^{2-}$ complex, which carries 2 electric charges on 9 atoms. The relatively higher need for hydration by the Rh complex allows the $Pt(CN)_4^{2-}$ to be more strongly extracted onto SIR than the highly hydrated Rh complex (Cortina *et al.*, 1998). Applying the oxidative acidic dissolution with aqua regia to the recovery of Rh from scrap is not highly successful, as Rh dissolves very slowly, even in aqua regia. The recovery requires high-energy inputs and strong acids. Kayanuma *et al.* (2004) found that the addition of reactive metals such as Mg and Ca in vapour form to a PGM, e.g. Pt, results in a complex such as RPt_xO_y, (where R is Ca or Mg) which dissolves easily in aqua regia, thereby enhancing dissolution.

Bhandare and Argekar (2002) have developed a low cost, very selective, energy saving separation process for the recovery of Rh and Pt from automotive catalyst leachates based on supported liquid membrane (SLM) technology. Separation is achieved by the transport of Pt and Rh from an aqueous HCl (with 20 % stannous chloride) solution into an HCl stripping solution, through a liquid membrane consisting of bis(2-ethylhexyl) phosphoric acid (HDEHP) in kerosene, supported on a polyvinylidene fluoride (PVDF) film. Lee and Tölg, (1993) developed a sorbent extraction system based on reversed-phase adsorption of complexed metals on a hydrophobic polymeric phase. The system shows much promise due to the selectivity enhancement owing to metal ions' different tendency to complex formation. Complete and rapid elution is possible from these sorbents, as the complexes are not chemically bound. But the resulting metal complexes may have low solubility in water, which may cause them to precipitate and cause the column to clog. Here, the use of a chelating agent e.g. bis(carboxymethyl)dithiocarbamate (CMDTC) to produce a water-soluble complex, would remove such a complication. For example, CDMTC chelates were adsorbed onto a polystyrene-divinylbenzene resin (XAD-4) in a column from acidic medium and eluted with ammonia solution. This type of system should work for Pt, Pd and Rh owing to dithio functional groups present in the CMDTC molecule (Lee and Tölg, 1993). Recovery via biological reduction of metals is well documented, e.g. the SRP, *Desulfovibrio desulfuricans*, reduced hexavalent uranium to stable UO_2. A hydrogenase enzyme was implicated in the reduction (Lloyd *et al*., 1998).

2.2 RHODIUM

Rhodium (Rh) was discovered in 1803 by W. H. Wollaston, in the black residue left after crude platinum had been dissolved in aqua regia. He named it for the Greek word ροδου (or rhodon) meaning “rose”, because of the rose colour commonly found in aqueous solutions of its salts (Greenwood and Earnshaw, 1989). Some of the properties of rhodium are summarized in Table 2.1. Rhodium is extremely inert to acids, even aqua regia. Dissolution of the metal is best effected by fusion with $NaHSO_4$. Rhodium will also react with oxygen and halogens at red heat, but only slowly. The most common oxidation states are the +1 and +3 states, with square planar and octahedral stereochemistry, respectively (Greenwood and Earnshaw, 1989).

Table 2.1 Some properties of Rhodium (Rh) (Greenwood and Earnshaw, 1989).

Property	Value
Atomic number	45
Number of naturally occurring isotopes	1
Atomic weight	102.9055
Electronic configuration	$[Kr]4d^8 5s^1$
Electronegativity	2.2
Metal radius (12 coordinate) / pm	134
Effective ionic radius (6 coordinate) / pm	
V	55
IV	60
III	66.5
Melting point (°C)	1960
Boiling point (°C)	3760
Density (20°C)/g.cm^{-3}	12.39

According to Greenwood and Earnshaw (1989), the complexes of rhodium(III) are usually derived, either directly or indirectly from the fully aquated species, $RhCl_3.3H_2O$. Figure 2.3 approximately indicates the lability of rhodium(III) towards aquation in solutions of lower chloride concentration. As the concentration of chloride increases, so does the concentration of the $RhCl_6^{3-}$ ion, while all aquated species decrease in concentration as the chloride concentration increases.

The labile character of rhodium towards aquation is not only dependent on the chloride content of the environment. The age of the solution also affects the Rh species found in a solution, i.e. as the solution ages, species of the type $[RhCl_{6-x}(H_2O)_x]^{x-3}$ (x = 1 to 6) are formed. Equations 2.1, 2.2 and 2.3 show the stepwise aquation of the $RhCl_6^{3-}$ anion. These species tend to react at different rates with a ligand and produce different complexes with varying extractability. For example, in the extraction of Rh as a thiocyanate complex by polyurethane foam, a one-day old solution contained mostly Rh of the species $[RhCl_5(H_2O]^{2-}$. This species was extracted with 92 % efficiency. In contrast, a seven-month old solution contained Rh of the species $RhCl_3(H_2O)_3$. Only 78 % of this species was extracted (Al-Bazi and Chow, 1984).

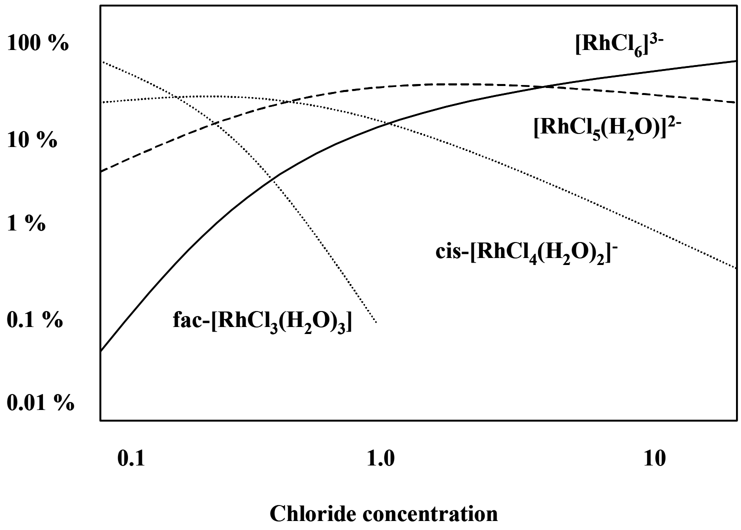


Figure 2.3 Approximate Rh species makeup of solutions containing varying chloride concentrations (adapted from Benguerel *et al.*, 1996).

$$[RhCl_6]^{3-} \leftrightarrow [RhCl_5(H_2O)]^{2-} + Cl^- \quad [2.1]$$

$$[RhCl_5(H_2O)]^{2-} \leftrightarrow [RhCl_4(H_2O)_2]^{-} + Cl^- \quad [2.2]$$

$$[RhCl_4(H_2O)_2]^{-} \leftrightarrow [RhCl_3(H_2O)_3] + Cl^- \quad [2.3]$$

Al-Bazi and Chow (1984) also determined a trend for the PGMs regarding their character towards forming extractable species, Pd > Pt > Ru > Rh > Ir. The trend shows that palladium and platinum form extractable species most easily, while rhodium and iridium are not easily converted to extractable species.

2.2.1 THE RELATIONSHIP BETWEEN pH AND THE PRECIPITATION OF RHODIUM IN PURE SOLUTIONS AND IN THE WASTEWATER

Three 100 ml samples of wastewater and three of pure rhodium solution (equivalent concentration to wastewater) were placed in 250 ml Schott bottles. Aliquots of 1 ml of 1 M NaOH were added to all bottles, after which the sample pHs were allowed to equilibrate for 24 hours. A 1 ml sample was extracted from each bottle after 24 hours, the pH of each bottle was noted, and the process was repeated until the pH of the bottled solutions reached approximately 12. Sample blanks were treated in an identical fashion except that distilled water replaced the 1 M NaOH solution. All samples were filtered through 0.45 µm pore size filters (Whatman, England) and the pH adjusted to < 2. The metal content from each sample was determined via atomic absorption spectrophotometry (GBC 909 AA, Avanta, Australia) and the results were used to compare the relative rates of precipitation of rhodium in each solution (i.e. wastewater and pure solution).

In Figure 2.5, it can be clearly seen that the wastewater showed more resistance to pH change than the pure rhodium solution did. Both solutions showed little change prior to the addition of 5 ml of 1 M NaOH. After 5 ml was added, the rhodium solution pH rose from just more than 2, to greater than 12, whereas the rise in pH seen in the wastewater was much more gradual, only reaching pH 8 after 8 ml of NaOH had been added. The wastewater pH then reached a plateau and did not exceed 9, despite the addition of a further 9 ml of NaOH.

When determining the degree of precipitation of rhodium dependent on the pH of the solution, it is obvious that the most rhodium was precipitated within the same timeframe as the rapid pH changes occurred (Figure 2.6). Approximately 100 % of the rhodium was precipitated out of the pure rhodium solution between additions 5 and 6 of 1 ml NaOH. Again, the wastewater showed greater resistance to changes resulting from pH alterations and precipitated approximately 80 % of the rhodium in solution between additions 6 and 8 of 1 ml NaOH.

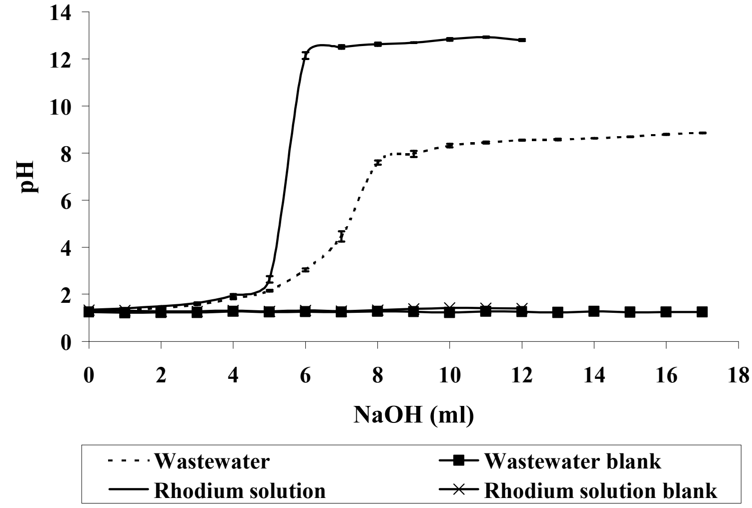


Figure 2.5 A titration of a rhodium solution and the wastewater to determine the relative resistance to pH changes caused by the addition of alkaline reagents, e.g. NaOH.

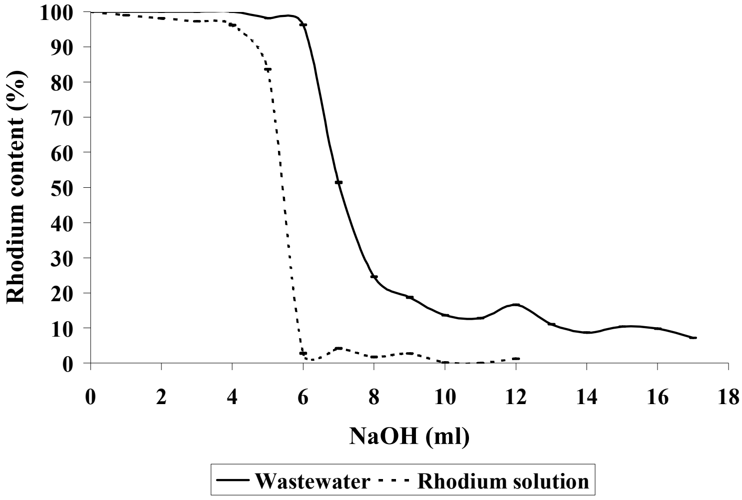


Figure 2.6 Precipitation of rhodium ions from a pure rhodium solution and from the wastewater in response to increasing pH.

The titration of the wastewater showed that there is a significant buffering capacity present within the wastewater, which may be helpful in preventing the spontaneous and unselective precipitation of all of the metals present in the wastewater. This suggests that the current method used for non-selectively removing all metals from the wastewater (the addition of a caustic agent) is not cost-efficient, as the wastewater requires a large dose in order to begin precipitation of the metals. On the other hand, this may represent an advantage when pH change is considered for the selective recovery of rhodium from the wastewater, in that the slow pH increase to the point of spontaneous precipitation makes the control of the wastewater pH at that point much easier. This has positive implications for novel processes such as nucleated precipitation (Chapter 4), where the addition of sufficient Na_2CO_3 is required to begin precipitation without initiating spontaneous precipitation of all of the rhodium at once, which would lead to discrete precipitation.

These results also indicate that the environment within the wastewater cannot be modelled to exact standards by a pure solution. There is, however, a large enough similarity for the pure solution to be an approximate guide to how the rhodium in the wastewater may react in certain instances.

2.3 HARD AND SOFT ACID-BASE THEORY

Of all chemical reactions, the generalized acid-base reaction (Equation. 2.4) is probably the most important:

$$A + :B \leftrightarrow A:B \qquad \textbf{[2.4]}$$

A is called a Lewis acid or electron acceptor, and :B is the Lewis base, or electron donor. A:B is the complex formed between them as a result of a partial donation of electrons from :B to A. Examples of such complexes include complexes and coordination compounds in which A is a metal atom or ion. When A is a metal ion, the base :B is called a ligand (Pearson, 1966).

Early research showed that metals fell into two categories, depending on the kinds of bases with which they prefer to coordinate. Schwarzenbach (1961) divided all metal ions into two groups, class **A** and class **B**, depending on the state of the *d*-orbitals of the metal. Typical class **A** metals were those without *d*-orbital electrons, and class **B** metals contained 8 to 10 *d*-orbital electrons occurring near the end of a transition series. Ahrland *et al*. (1958) categorized the metal ions according to the formation of stable complexes, i.e. class *a* metals formed stable complexes with the first ligand atom of each Periodic group (N, O, F), while class *b* metals formed stable complexes with the second or subsequent ligand atoms. Figure 2.4 shows a stylized Periodic table highlighting the classes defined by Ahrland *et al.* (1958).

The figure shows that all class *b* cationic acceptors (in their normal valence states) were found together in a vaguely triangular shape. The base of the triangle stretches from approximately tungsten (W), in the sixth Period, to polonium (Po), and has its apex in the first Period, at copper (Cu). Metals showing the most pronounced class *b* character include Cu(I), Rh(I), Pd(II), Ag(I), Pt(II) and Hg(II). The boundary area, though, is diffuse, as the various oxidation states of the borderline elements have different characters, e.g. Cu(I) is in class *b*, but Cu(II) is a borderline oxidation state (Ahrland *et al.*, 1958).

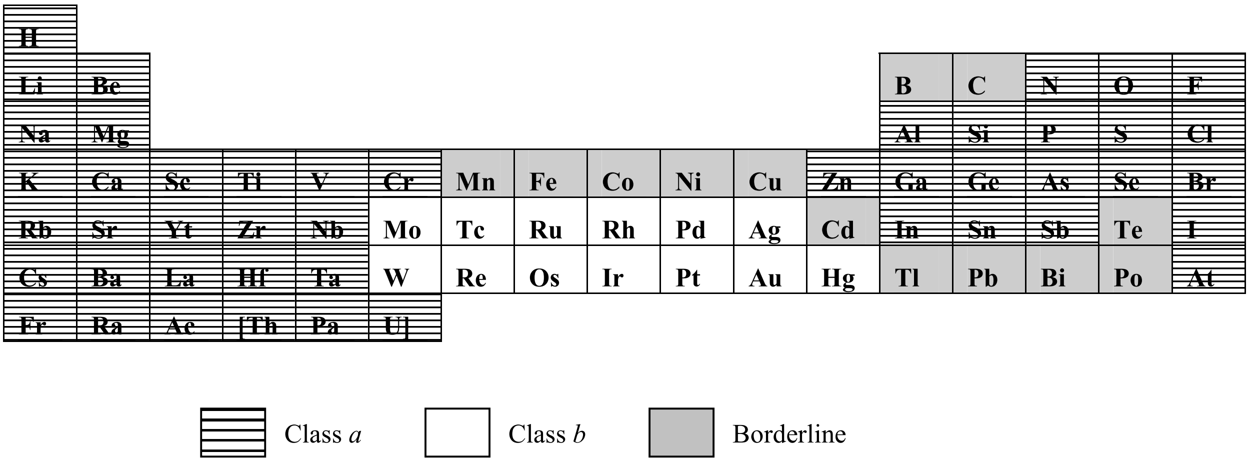


Figure 2.4 Classification of acceptor atoms in their normal-valent states (Ahrland *et al.*, 1958).

The Ionic-Covalent theory of Grimm and Sommerfeld (Pearson, 1966) provides an indication as to why metal ions fall into these two distinct categories. Hard acids are assumed to bind bases primarily by ionic forces. A high positive charge and small size favour such binding. Bases of large negative charge and small size are held most tightly. Soft acids bind bases primarily by covalent bonds. For good covalent bonding, the two bonded atoms should be of similar size and similar electronegativity. For many soft acids ionic bonding would be weak or non-existent because of the low charge or absence of charge.

To summarize thus far, a soft base is defined as having a donor atom of high polarizability and low electronegativity and is easily oxidized or is associated with empty, low-lying *d*-orbitals (i.e. a base in which donor electrons are not held tightly but can be easily distorted or removed. A hard base exhibits low polarizability and high electronegativity, is hard to reduce and is associated with empty orbitals of high energy and hence, inaccessible. A hard acid (class *a*/A) is either a metal or non-metal of small size and high positive oxidation state. In addition, they are characterized by the absence of any outer electrons that are easily excited to higher states. All of these characteristics lead to an overall characteristic of low polarizability. Conversely, a soft acid (class *b*/B) exhibits low or zero charge, a larger size, and several easily excited outer electrons, i.e. high polarizability.

Pearson (1968a) condensed these phenomena into a simple statement, known as the Theory of Hard and Soft Acids and Bases (HSAB); "Hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases". According to Pearson (1967), the first person to notice an example of hard and soft was Berzelius, who noted that some metals occurred as ores of oxides and carbonates and some occurred primarily as sulphide ores. The oxide and carbonate ores were hard acids such as Mg, Al, and Ca. The sulphide ores were soft acids such as Cu, Hg, and Pb. Tables 2.2 and 2.3 illustrate the categorization according to Pearson's theory. In Table 2.2, the hard, soft, and borderline bases are shown and Table 2.3 shows the hard, soft, and borderline acids.

Table 2.2 Categorization of hard, soft and borderline bases (Pearson, 1968a).

Hard	Soft	Borderline
H_2O, OH^-, F^-	R_2S, RSH, RS^-	$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^-, N_2
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$	
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$	
ROH, RO^-, R_2O	CN^-, RNC, CO	
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6	
	H^-, R^-	

So, if A is soft, the order of decreasing base strength for various donor atoms is approximately:

$$S > C \sim P > I > Br > Cl > N > O > F,$$

meaning that soft A will bind preferentially with donor atoms on the left, and if A is hard, the order is strongly inverted (Pearson, 1967).

Occasionally, metal ions show soft behaviour despite being of high positive charge, e.g. Pt(IV). This can be explained in terms of the actual charge on the metal ion rather than the formal charge, for example, there is evidence that the Pt ion in PtI_6^{2-} has a charge near zero and not +4. It has been noted that in cases such as these where a high oxidation state leads to soft behaviour that the ligands involved are soft. The covalent bonding that takes place results in a large transfer of charge from the ligands to the metal, which leads to extensive charge neutralization on the metal ion, i.e. low to zero charge character of a soft acid (Pearson, 1966).

Rhodium(III) is classed as a borderline acid in Table 2.3. However, the division between borderline and soft metals is less clearly defined than the division between borderline and hard metal (Avery and Tobin, 1993). It may thus be assumed that Rh^{3+} is a borderline/soft metal and will preferentially covalently bind soft donor atoms in a similar way to that suggested for Pt(IV) by Pearson (1966).

Table 2.3 Pearson's categorization of hard, soft, and borderline acids (Pearson, 1968a).

Hard	Soft	Borderline
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, $Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+}	
Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	Tl^{3+}, $Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$	Rh^{3+}, Ir^{3+}, $B(CH_3)_3$, SO_2, NO^+, Ru^{2+}, Os^{2+}, R_3C^+, $C_6H_5^+$, GaH_3
N^{3+}, Cl^{3+}, Gd^{3+}, Lu^{3+}	$GaCl_3$, GaI_3, $InCl_3$	
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, CH_3Sn^{3+}	RS^+, RSe^+, RTe^+	
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}	I^+, Br^+, HO^+, RO^+	
Pu^{4+}, Ce^{3+}, Hf^{4+}, WO^{4+}, Sn^{4+}	I_2, Br_2, ICN, etc.	
UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+}	Trinitrobenzene, etc.	
$BeMe_2$, BF_3, $B(OR)_3$	Chloranil, quinines, etc.	
$Al(CH_3)_3$, $AlCl_3$, AlH_3	Tetracyanoethylene, etc.	
RPO^{2+}, $ROPO^{2+}$	O, Cl, Br, I, N, RO^-, RO_2^-	
RSO^{2+}, $ROSO^{2+}$, SO_3	M^0 (metal atoms)	
I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}	Bulk metals	
RCO^+, CO_2, NC^+	CH_2, carbenes	
HX (hydrogen bonding molecules)		

So many phenomena can influence the strength of binding between atoms that it is unlikely that a single scale of intrinsic acid-base strength or of hardness-softness, can exist. It has been a great temptation to scientists to try to equate softness with some easily identifiable physical property such as redox potential, ionization potential, or polarizability. All of these give approximately the same order, but not exactly the same, and none is suitable as an exact measure. The convenient term micro-polarizability is sometimes appropriate as a replacement for softness as an indication that deformability of an atom, or group of atoms, at a bonding distance is the important property (Pearson, 1968a).

So, why does the HSAB theory seem to work? As Pearson (1967) states, it is a statement of scientific fact, not a theory in itself. There must be underlying theories that explain these facts. He is certain, however, that these theories will not be simple, since to explain the stability of the acid-base complex A:B consideration of all the effects that determine the strength of chemical bonds generally is required, i.e. all the theory of chemical bonding must be used. Thus, the HSAB principle represents a simple but imprecise law with a very wide range of applicability in spite of the lack of precision. The considerable utility of the principle can be applied in prediction, but perhaps more importantly, to correlating the vast amount of chemical information regarding acid-base binding already at hand (Pearson, 1968b).

2.4 SUMMARY AND CONCLUSIONS

Rhodium is a precious metal of immense, and growing worth and new applications of the metal are still being discovered owing to its unique properties. Rhodium(III) is classed according the HSAB theory as a borderline metal, possibly with a tendency towards a soft character. This implies that complexes of rhodium are bound preferentially by borderline and soft bases, e.g. those including atoms such as S, C and P.

The wastewater is characterized by extremely high chloride content, so it can be assumed that the rhodium present in the form of chloro-complexes. These complexes have a tendency, depending on the age and chloride content of the solution, to become aquated. The more aquated the species, the harder it becomes to extract from the solution. Heating or the addition of a catalyst has been suggested as a method for the reversal of the aquation and the conversion of the unextractable species to more extractable ones.

The mining and refining processes that yield rhodium metal are extremely efficient (99.95 %), however, the recovery of the final 0.05 % of the metal value is becoming more important as the value of the metal increases. Current practices do not allow for the selective recovery of rhodium from process effluents and most is precipitated as sludge in slime dams on refinery property. A number of novel technologies show promise in terms of selectivity and efficiency; however, they are often complex and costly, requiring large amounts of capital funding and specialised training. They also may not be efficient when challenged with a wastewater such as this, with a high organic content and low pH, with only a dilute concentration of rhodium.

Biological systems such as the EMBR described in Chapter 3 may be capable of selectively precipitating rhodium ions from the wastewater without adversely affecting the SRP culture responsible for the sulphide production. A simple chemical process such as nucleated precipitation (Chapter 4) that requires no viable (or even non-viable) organisms may also be applicable in this case. Biosorption (Chapter 5) is a well-documented biological phenomenon, which, due to the use of non-viable biomass, could also be applied to the wastewater in an attempt to recover the rhodium in a form suitable for further refining.

HYPOTHESIS, AIMS AND OBJECTIVES

HYPOTHESIS

Rhodium(III) metal ions can be recovered from precious metal refinery wastewater by using a low-cost, low maintenance biological process.

AIMS AND OBJECTIVES

AIMS

To screen three low-cost technologies for the ability to efficiently recover rhodium(III) ions from a precious metal refinery wastewater.

To select one of the three processes screened as a potential case for further optimization in a later study.

OBJECTIVES

1. Determine the efficiency with which a sulphide-extraction membrane bioreactor can recover rhodium(III) ions from a precious metal wastewater.
2. Determine the efficiency with which a fluidized sand bed reactor can recover rhodium(III) ions from a precious metal wastewater.
3. Determine the efficiency with which an immobilized yeast biosorbent can recover rhodium(III) ions from a precious metal wastewater via passive biosorption.
4. Identify possible problems inherent in each technology.
5. Make recommendations regarding the choice of process to be optimized.

CHAPTER 3

MEMBRANE TECHNOLOGY TO RECOVER RHODIUM(III) FROM PRECIOUS METAL REFINERY WASTEWATER

3.1 INTRODUCTION

The coupling of a membrane to a bioreactor has attracted a large amount of attention in recent years, both academically and commercially. This is due to the advantages this hybrid process offers over conventional biological wastewater treatment systems (van Houten *et al.*, 2001; Visvanathan *et al.*, 2000). Hybrid processes have emerged as viable alternative wastewater treatment processes in areas where space (for settling ponds, etc.) and water resources are limited and are also gaining popularity as alternatives when treating industrial wastewaters with high total dissolved solids, where settling and clarification are often a problem (Enegess *et al.*, 2003; van der Roest *et al.*, 2001).

Biomass separation membrane bioreactors are the most common type of membrane bioreactor (MBR). These MBRs can be considered a combination of a suspended growth reactor and a membrane filtration device. The benefits of these solid-separation membrane bioreactors are superior to most (if not all) non-membrane-based separation techniques. The permeate from the membrane is typically free from solids and macro-colloidal material and it is possible to obtain complete retention of all suspended matter including bacteria and viruses, making the water safe for discharge into the receiving environment (Stephenson *et al.*, 2000). de Korte *et al.* (2001) state that, along with the complete removal of bacteria and viruses, MBRs should significantly reduce heavy metal and organic micropollutant (such as pesticide and polyaromatic hydrocarbon) loads. A smaller footprint is attainable with an MBR system, as the single filtration step takes the place of a conventional multi-stage process involving primary settlement, secondary biological treatment and a possible polishing step (Gander *et al.*, 2000).

The membrane aeration bioreactor (MABR) concept was developed in response to the need for increased oxygen mass transfer into wastewaters in cases where the oxygen requirements for degradation of the pollutant are too high for conventional aeration processes. It is also applicable when the possibility exists that the bubbling of air would result in either the stripping of volatile organic carbons or of foaming of industrial wastewaters (Pankhania *et al.*, 1999). The membrane itself can play a dual role in the reactor, namely:

- As a means for supplying oxygen and
- As a substrate for support of biofilm formation.

Membrane aeration bioreactors have been use to treat a wide variety of wastewater types and have been shown to be particularly effective in treating high oxygen demanding wastewaters (Yamagiwa and Ohkawa, 1994), biodegradation of volatile organic compounds (Kniebusch *et al.*, 1990), combined nitrification (Timberlake *et al.*, 1988), denitrification and/or organic carbon degradation in a single biofilm (Hirasa *et al.*, 1991).

Biological degradation of the toxic organic compounds in wastewaters is well understood and appears to be the ideal solution to the reduction of these emissions into the environment. However, a number of factors complicate this. A major factor is the complex nature of the final wastewater as it leaves the process; this includes the number and variety of organic compounds and the composition of the inorganic fraction (salts, acids, bases, metal salts) (Livingston *et al.*, 1996; 1998). Others include the presence of recalcitrant pollutants that simply pass through the treatment system and the possible stripping of volatile organic compounds into the atmosphere (Freitas dos Santos *et al.*, 1995; Brookes and Livingston, 1994).

A seemingly obvious solution to these problems would be to bioaugment the existing microbial cultures in the wastewater treatment plant with specialized cultures capable of degrading toxic, recalcitrant pollutants as they pass through the plant. However, studies on specialized cultures such as would be required have concentrated on degradation in ‘ideal’ conditions, where the only pollutant present is that to be degraded, and the growth medium is carefully controlled to supply maximal nutrient requirements in order for the culture to survive and degrade efficiently. This has translated to difficulties arising when the culture is faced with ‘real’ industrial conditions (Livingston, 1994). Thus, the problem faced can be summarized as provision of conditions suitable for biodegradation of toxic organic pollutants discharged as components of complex wastewater streams that may inhibit the growth and efficacy of the specialized culture. The problem described led to researchers developing a membrane bioreactor capable of solving this problem, the extractive membrane bioreactors (EMBR). Most work focused on the implementation of EMBRs has been with regard to chemical industry wastewaters and the toxic organic compounds present therein (Livingston, 1994).

The principle of an EMBR is illustrated in Figure 1.7. An industrial wastewater containing the organic compound to be degraded is passed over one surface of a selectively permeable membrane, while a microbial culture is maintained in an aqueous biomedium at the other surface. The pH and ionic strength of the wastewater have no influence on the makeup of the biomedium, as the membrane is effectively impermeable to any inorganic or charged species in the wastewater. Thus the biomedium conditions can be controlled to provide optimal growth conditions for the microbial culture in spite of the biologically hostile makeup of the wastewater (Livingston *et al*., 1998).

Studies involving synthetic wastewater streams at laboratory scale have yielded highly successful results. Freitas dos Santos and Livingston (1994) reported a > 99 % removal of 1,2-dichloroethane from an initial concentration of 1600 mg/L. 2,4-Dichlorophenoxyacetic acid, a component of commercial herbicides, has also been successfully degraded at laboratory scale using a suitably acclimated microbial culture (Buenrostro-Zagal *et al*., 2000). Jorge and Livingston (2000) found that the two most commonly used solvents in the chemical and pharmaceutical industries; toluene and dichloromethane were possibly being degraded by a commensal microbial culture. When the EMBR is used with industrial wastewaters, the results are equally encouraging. Wastewater from a 3-chloronitrobenzene-manufacture plant was successfully remediated with removal efficiencies of greater than 99 % achieved at residence times of approximately 30 minutes (Brookes and Livingston, 1994). Brookes and Livingston (1995) operated a lab-scale reactor continuously for 5 months and consistently removed aniline, 4-chloroaniline, 2,3-dichloroaniline and 3,4-dichloroaniline at efficiencies greater than 99 %.

Other successful studies include the removal and degradation of compounds such as monochlorobenzene, in which an EMBR destroyed 98 to 99 % of the pollutant at a flow rate of 50 L/h (Livingston *et al*., 1998), 1,2-dichloroethane (94.5 % removal) with negligible air-stripping

(Freitas dos Santos and Livingston, 1995) and various other chemical and pharmaceutical waste streams with similar results.

A number of variations on the EMBR configuration have also been tested. Lui *et al.* (2001) showed the efficiency of the EMBR in a liquid-liquid extraction configuration by degrading chlorophenolic compounds such as 2,4,6-trichlorophenol, 2,4-dichloroaniline and pentachlorophenol to levels lower than 100 μg/L. The degradation of a waste gas stream containing 1,2-dichloroethane was investigated by Freitas dos Santos *et al.* (1995) and resulted in removal of 91 % of the pollutant.

Metal industry wastewaters usually contain organic and inorganic compounds that may be toxic or inhibit the growth of microorganisms. They are also often saline or exhibit extremes of pH. Conventional technologies for the removal of metals from such wastewaters include precipitation, ion exchange, and adsorption; however, this description fits that of a wastewater suitable for treatment via EMBRs.

Precipitation is often the conventional method of choice for metal removal, usually with precipitants such as lime, which are expensive over the long term, require trained operators, and produce large volumes of sludge. The most effective precipitant is sulphide, because it precipitates metals regardless of the characteristics of the wastewater and is far less pH dependent than hydroxide. Sulphide as a precipitant does have its disadvantages, such as the toxicity and odour of H_2S. In addition, the corrosion, safety and handling complications as well as the expense of using chemically produced H_2S are often considered prohibitive.

Biological production of H_2S is already considered a conventional method of precipitating metals from wastewaters. In this method sulphate-reducing prokaryotes (SRP) are grown in direct contact with the wastewater. Microbial reduction of sulphate to sulphide provides the H_2S, which then precipitates metal ions dissolved in the water. These metal sulphides are insoluble and can thus be easily separated. This application is limited by the inhibition of microbial activity due to the biologically hostile characteristics of the wastewater. An EMBR system can be used to solve these limitations by preventing direct contact between the SRP and the wastewater. Figure 3.1 illustrates the principle of the EMBR-SRP. This system will be tested as a possible means of recovering rhodium(III) metal from precious metal refinery (PMR) process wastewaters.

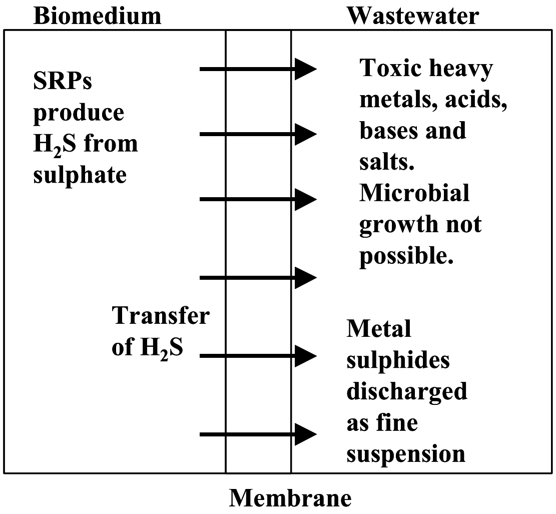


Figure 3.1 A schematic diagram of the EMBR-SRP treatment system. A silicone membrane separates the two aqueous phases, allowing H_2S to permeate from the biomedium phase into the wastewater and so precipitate the metal. Charged species in the wastewater cannot permeate the membrane, making it possible to pass highly inhibitory wastewaters through the membranes without inhibiting the SRP (Chuichulcherm *et al.*, 2001).

3.2 HYPOTHESIS

The extractive membrane bioreactor-sulphate reducing prokaryote (EMBR-SRP) system, hereafter known as the Sulphide Extraction Membrane Bioreactor (SEMB) is capable of efficiently recovering rhodium(III) metal from process wastewaters by precipitation as a metal sulphide.

3.3 AIMS AND OBJECTIVES

The overall aim was to investigate the efficacy and applicability of the SEMB for the recovery of rhodium(III) from process wastewaters. In order to achieve this, the following three objectives were set:

- Maximize sulphide mass transfer in order to maximize rhodium sulphide formation and precipitation
- Determine the applicability of the process using various base and precious single metal solutions.

- Conduct a bench-scale trial using the industrial wastewater described in Chapter 2.

3.4 MAXIMIZATION OF H_2S MASS TRANSFER THROUGH SILICONE MEMBRANES

Figure 3.1 illustrates the principle of the SEMB, in which H_2S generated by a consortium of SRP passes through the gas-permeable membrane along a concentration gradient and precipitates the metal ions as metal sulphides. For optimal mass transfer of the gas through the membrane, it must be in a dissolved, non-dissociated form. This species dominates at low pH (Figure 3.2).

On the wastewater side of the membrane, dissociated sulphide species (HS^- and S^{2-}) are required for interaction with and precipitation of metal ions. S^{2-} is disregarded in general, as the dissociation constant is extremely low and excludes its formation at pH values lower than 14. Thus, the HS^- form is dominant at pH > 6. Therefore, for optimum process efficiency, the sulphide gas must pass from a low pH medium (< 5) to a higher pH wastewater (> 6). However, SRP are generally neutrophilic, preferring a medium pH of 5.5 to 8. This poses a problem, as for optimum operation, both the sulphide generating medium and the wastewater pH need to be adjusted and this may prove to be disadvantageous as the increased costs incurred with these changes may make the technology financially non-viable.

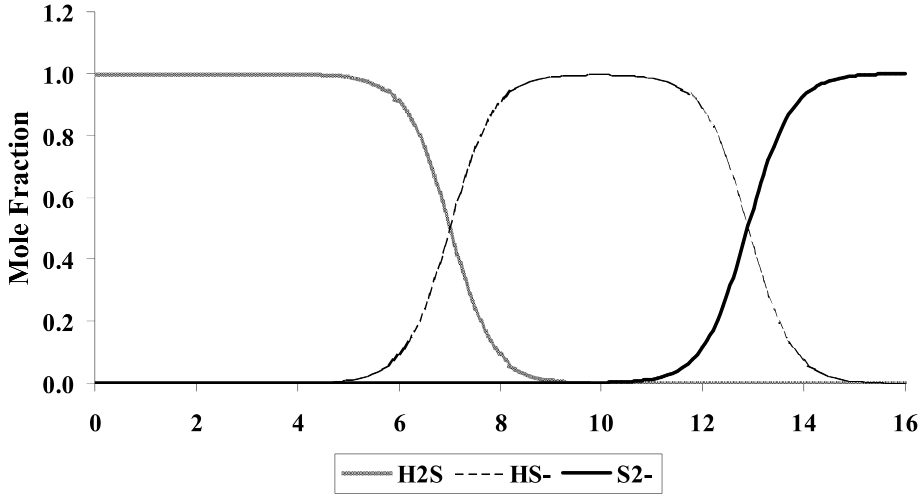


Figure 3.2 Sulphide speciation as a function of pH.

3.4.1 MATERIALS AND METHODS

Sulphate-reducing consortium

A pre-existing laboratory fed-batch SRP (original inoculum from Grootvlei Mine, Gauteng) anaerobic digester (Figure 3.3) (25 L, low rate, mesophilic) was maintained on a modified Postgate medium (Sodium lactate (60 % solution), 6 ml; $MgSO_4.7H_2O$, 2.0 g; NH_4Cl, 1.0 g; Na_2SO_4, 1.0g, yeast extract, 1.0 g; K_2HPO_4, 0.5 g; $CaCl_2.2H_2O$, 0.1g; in 990 ml, add ascorbic acid, 0.1 g and sodium thioglycollate, 0.1 g; in 10 ml (Atlas, 1993)). Twice weekly, 5 L of supernatant was removed from the reactor and replaced with 5 L of fresh medium. This supernatant was utilized as a source of biogenic sulphide.

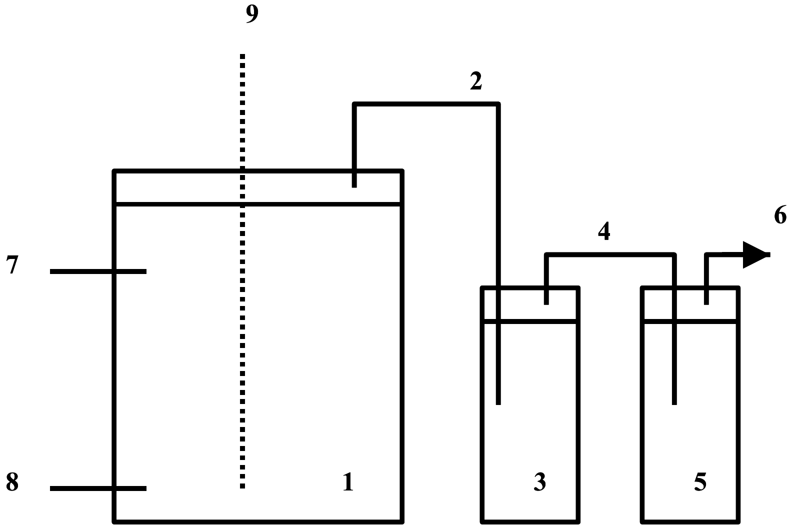


Figure 3.3 SRP anaerobic digester maintained on modified Postgate medium. 1. SRP bioreactor. 2. Gas outlet. 3. Zinc(II) acetate trap. 4. Gas outlet. 5. Zinc(II) acetate trap. 6. Air outlet. 7. Supernatant outlet. 8. Biomass outlet. 9. Sampling port.

The apparatus used to analyse sulphide mass transfer through silicone membranes is depicted in Figure 3.4. Two 2.0 L borosilicate glass vessels were used as reservoirs. Gas-impermeable PVC laboratory tubing (6×10 mm) was used as inlet and outlet tubing. Laboratory-grade silicone tubing (3.5×5 mm) was used as a gas permeable membrane. Two pumps were used, one for high flow rates (Watson Marlow 504 S, England) and one for low flow rates (Ismatec, Switzerland).

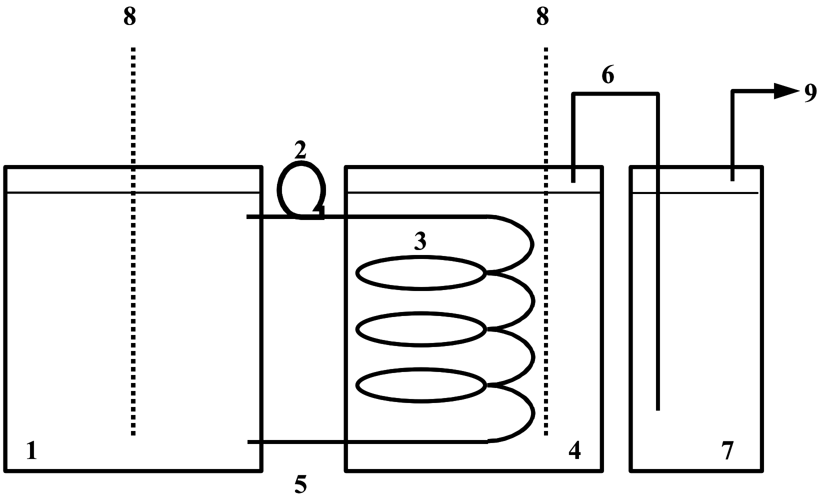


Figure 3.4 Sulphide mass transfer apparatus. 1. Receiving water reservoir. 2. Peristaltic pump. 3. Silicone membrane. 4. Supernatant reservoir. 5. Outlet tubing. 6. Gas outlet. 7. Zinc(II) acetate trap. 8. Sampling ports. 9. Air outlet.

Optimization of pH conditions

All pH experiments were performed in a sealed vessel containing 2 L of supernatant by submerging a 3×5 mm diameter silicone tube (Carlin Medical Extrusions, South Africa) (2 m length) attached at an inlet and outlet point. Deionized water was pumped through the tube and the total dissolved H_2S levels were monitored in both the water and the supernatant. At regular intervals, samples were taken from both the receiving water and supernatant. These were analyzed for total sulphide concentration (Spectroquant kit 1.14779 and Spectroquant Nova 60, South Africa) and pH (Cyberscan 2500, Eutech Instruments, Singapore). When necessary, initial pH adjustments were made to the supernatant and/or receiving water using 3 M hydrochloric acid (HCl) or 1 M sodium hydroxide (NaOH). Agitation experiments were performed using a magnetic stirrer (Agimatic-N, JP Selecta, Spain) with a stirrer bar placed inside the vessel containing the supernatant.

Calculation of overall mass transfer coefficient, k_{ov} (Chuichulcherm et al., 2001)

H_2S flux across the membrane can be written as:

$$N = k_{ov}(C_{s,t} - C_{r,t}) \quad \textbf{[3.1]}$$

The overall mass transfer coefficient of H_2S through the membrane can be estimated using the following mass balance on the system

$$-V\frac{dC_{s,t}}{dt} = k_{0v}A(C_{s,t} - C_{r,t)} \qquad \textbf{[3.2]}$$

Assume at steady state:

- Volumes of solutions are equal.
- No H_2S adsorbed into membrane.
- No reaction occurred in tube.
- Negligible H_2S in membrane itself.

The sum of the concentration of H_2S in the medium and receiving solution at any point is equal to the total concentration:

$$C_{r,t} = C_{s,o} - C_{s,t} \qquad \textbf{[3.3]}$$

Substituting equation 3.3 into equation 3.2 gives:

$$-V\frac{dC_{s,t}}{dt} = k_{ov}A(2C_{s,t} - C_{s,o}) \qquad \textbf{[3.4]}$$

Integration of equation 3.4 gives:

$$\frac{1}{2}[\ln(C_{s,o}) - \ln(2C_{s,t} - C_{s,o})] = \frac{k_{ov}A}{V}t \qquad \textbf{[3.5]}$$

A plot of 0.5 [$\ln(C_{s,o}) - \ln(2C_{s,t} - C_{s,o})$] against t yields a straight line with a slope of $k_{ov}A/V$, where A and V are known, thus k_{ov} can be calculated.

3.4.2 RESULTS

Figure 3.5 shows the sulphide profile of the system with pH unadjusted (Experiment 1). The pH of the supernatant and the receiving water were 7.85 and 6.83, respectively. The rate of transfer of sulphide from the supernatant into the receiving water was such that the concentration never reached more than approximately 10 mg/L in the receiving water. However, the supernatant lost approximately 20 mg/L over the 28-hour experiment. This discrepancy is possibly explained by adsorption of sulphide onto the membrane or vessel surfaces or by small amounts being lost to the vessel headspace. No zinc acetate trap was used in these experiments as the system was kept closed, and thus no loss of sulphide could be attributed zinc sulphide precipitation. The sulphide mass transfer coefficient was calculated as 1.47×10^{-6} m/s.

In the second experiment, the pH of both the supernatant and the receiving water were adjusted to approximately 3. The system reached equilibrium after 24 hours (Figure 3.6), with both the supernatant and the receiving water containing approximately 70 mg/L sulphide. The pH in both the supernatant and receiving water were monitored and at equilibrium, the supernatant pH had risen to 3.7 and that of the receiving water had dropped to 2.4. The calculated mass transfer coefficient for sulphide was three times that of experiment 1 (3.25×10^{-6} m/s).

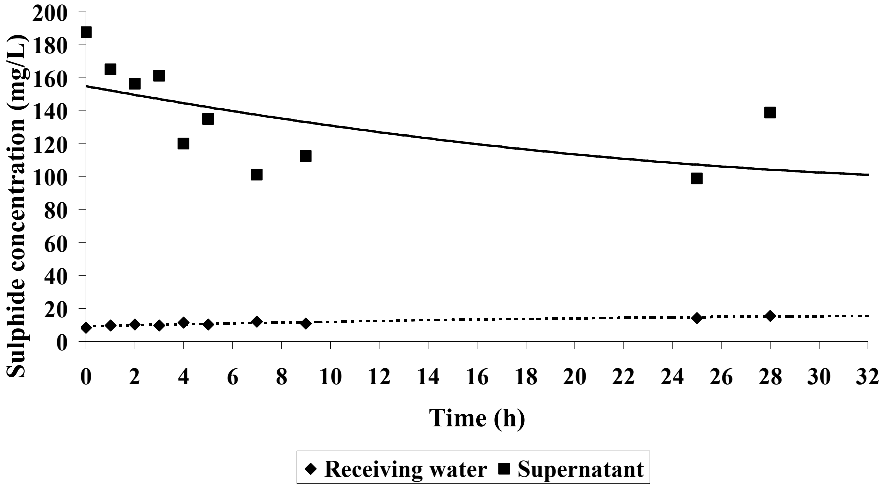


Figure 3.5 A sulphide profile of the SEMB system at ambient pH (experiment 1). Initial pH values of 6.83 (receiving water) and 7.85 (supernatant) were recorded.

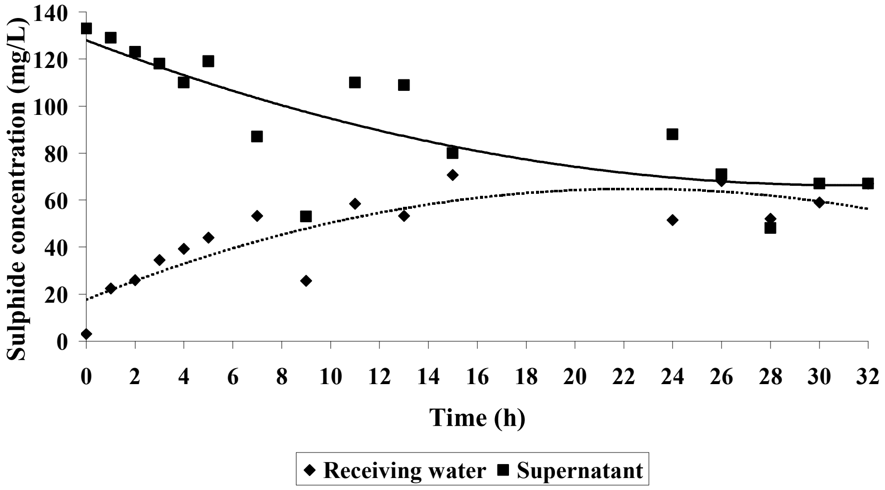


Figure 3.6 A sulphide profile with both receiving water and supernatant at pH 3. Equilibrium was reached at 24 hours, with both supernatant and receiving water concentrations of approximately 70 mg/L.

A third experiment (Figure 3.7) was performed at identical pH levels to that of experiment 2. The vessel containing the supernatant was stirred using a magnetic stirrer to maintain a high concentration gradient at the membrane: supernatant interface. This resulted in a mass transfer coefficient an order of magnitude larger than that achieved in experiment 2, namely 1.04×10^{-5} m/s for experiment 3 versus 3.25×10^{-6} m/s for experiment 2. The experiment was run for 5 hours rather than 24 as only the first five measurements were required to calculate overall mass transfer.

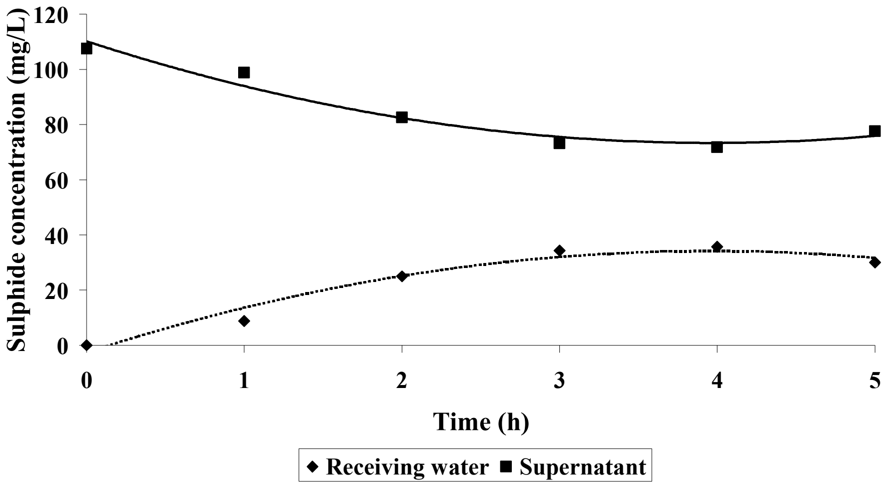


Figure 3.7 A sulphide profile of an agitated system. Both the supernatant and the receiving water were at a recorded pH of approximately 3.

In Table 3.1, the calculated overall mass transfer coefficients for each experiment are tabulated. The only major increase in mass transfer took place in experiment 3, in which the agitation of the system increased the mass transfer ten-fold.

Table 3.1 Tabulated results of the pH optimization experiments. (*Experiment 3 was performed at similar pH levels as experiment 2, however the vessel containing the supernatant was stirred to increase the sulphide concentration gradient at the membrane surface).

Experiment number	**pH**		**Mass transfer coefficient (m/s)**
	Supernatant	**Receiving water**	
1.	7.85	6.83	1.47×10^{-6}
2.	3.06	2.97	3.25×10^{-6}
***3.**	3.12	3.09	1.04×10^{-5}

3.4.3 DISCUSSION

The efficiency of the SEMB relies on the optimization of the mass transfer of sulphide across the membrane into the wastewater. Thus, an initial experiment using unadjusted supernatant and water was run to determine the basal overall mass transfer coefficient (k_{ov}) (1.47×10^{-6} m/s) for the system upon which to improve.

By lowering the pH of both the supernatant and the receiving water to below the pKa (6.8) of the sulphide ion (HS^-) in experiment 2, the sulphide equilibrium was shifted and allowed the dissolved gas form, H_2S to dominate (Chuichulcherm *et al.*, 2001). This also led to the expectation that monitoring of the single form would minimize the apparent loss of sulphide in experiment 1. This proved true, and an apparent equilibrium was reached with approximately 70 mg/L concentrations of sulphide in both solutions. A higher mass transfer coefficient was calculated from these results (3.25×10^{-6} m/s). The final pH of the system components showed a similar trend to that reported by Chuichulcherm *et al.* (2001), where the H_2S solution pH increased from 3 to 3.4 and the receiving solution pH decreased from 3 to 2.6. In the present study, the supernatant pH increased from 3.06 to 3.7 and the receiving water pH decreased from 2.97 to 2.4. The time taken to reach equilibrium also matched that reported by Chuichulcherm *et al.* (2001), as both the present experiment and experiments performed by the authors referred to attained equilibrium in approximately 24 hours.

Agitation of the supernatant to maintain a high concentration gradient at the membrane: supernatant interface resulted in a tenfold increase in mass transfer. This result is comparable to the results published by Chuichulcherm *et al.* (2001). In their study, the mass transfer coefficients achieved using three membranes of differing thickness were compared. The highest mass transfer was achieved with a membrane thickness of 0.24 mm (9.91×10^{-6} m/s) and the lowest (5.36×10^{-6} m/s) using membranes with 0.59 mm thickness. The membrane used in the present study was much thicker than any tested by Chuichulcherm *et al.* (2001) (1.5 mm), but the agitation seemed to more than compensate for the thicker membrane, as the overall mass transfer calculated from the agitation experiment was 1.04×10^{-5} m/s.

3.5 REMOVAL OF METAL IONS FROM SYNTHETIC SOLUTION BY SEMB

Metal solution experiments were conducted using base metal salts as a cost-efficient model for metal removal using the SEMB system. Zinc(II) was chosen to verify the data from the study as it had already been tested in a similar system and responded well (Chuichulcherm *et al.*, 2001). Copper(II) was chosen because, although not a platinum group element, it lies in close proximity to the group on the periodic table and may provide a useful indication of how the rhodium(III) ions may react, and the HSAB theory discussed in Chapter 2 classifies Cu(II) alongside Rh(III) in the borderline acid category, which may allow for further correlation between the reactions of the two metals. Finally, synthetic rhodium(III) solutions made up to concentrations equivalent to that found in real wastewater were tested.

3.5.1 MATERIALS AND METHODS

The system was set up as described in section 3.4.1. Base metal solutions were made up from corresponding metal salts ($ZnSO_4$ and $CuSO_4$, Merck, South Africa) of desired concentration in deionized water. Rhodium(III) solutions of the desired concentration were made up from an atomic absorption spectrophotometric standard solution (1000 mg/L, Fluka Switzerland) and diluted with deionized water. Atomic adsorption spectrophotometric standard solutions were prepared from the same 1000 mg/L standard solutions as mentioned above (zinc, copper, rhodium) and diluted with deionized water to the desired concentration. All glassware used was washed in 5 % nitric acid and subsequently rinsed in deionized water to remove any possible interference by metal ions adsorbed to the glassware surfaces. 3 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH) were used for pH adjustments.

Metal precipitation experiments

The pH of the supernatant was adjusted to pH 3 using 3 M HCl prior to initiating the experiment. Two litres of the relevant metal solution was circulated at a flow rate of 20 ml/min through the membrane for a minimum of 24 hours. Samples were taken from both the metal solution and the supernatant. All samples taken from the metal solution were immediately filtered through a 0.45 µm pore filter paper (nylon for zinc(II) and copper(II), cellulose acetate for rhodium(III) (Whatman, England) as experiments have shown that rhodium adheres to nylon filters and base metals adhere to cellulose acetate filters (data not shown)) to separate the precipitate from the sample. These samples were then assayed immediately for total sulphide (Spectroquant kit method and Spectroquant Nova 60 (South Africa)) and pH. The dissolved metal concentration was assayed using atomic absorption spectrophotometry (GBC 909 AA, Avanta, Australia).

Fouling amelioration

Attempts were made to remove the precipitate layer responsible for fouling the membrane in the copper and rhodium solution. These included physical (non-destructive and destructive), chemical, and system design methods. The physical methods included non-destructive backwashing at high velocities with the metal solution and destructive scraping of the inner membrane surface using a spatula. The chemical method involved acid resolubilization of the precipitate by passing 5 % solutions of either nitric or hydrochloric acids through the membrane for two to three hours, with frequent backwashes and velocity changes. The design parameter changed was the length and inner diameter (2 m of 3.5×5 mm replaced with 1 m of 6×10 mm (Carlin Medical Extrusions, South Africa)) of the tubing constituting the membrane in an attempt to increase the turbulence within the membrane.

3.5.2 RESULTS

The supernatant was acidified to pH 3, and the metal solution was left unchanged (pH 5.6) as attempts to adjust it in either direction resulted in spontaneous precipitation of the zinc(II) ions. The pH of the metal solution decreased steadily from 5.6 to 2.3 after 24 hours (Figure 3.8), while that of the supernatant remained constant at approximately 3.

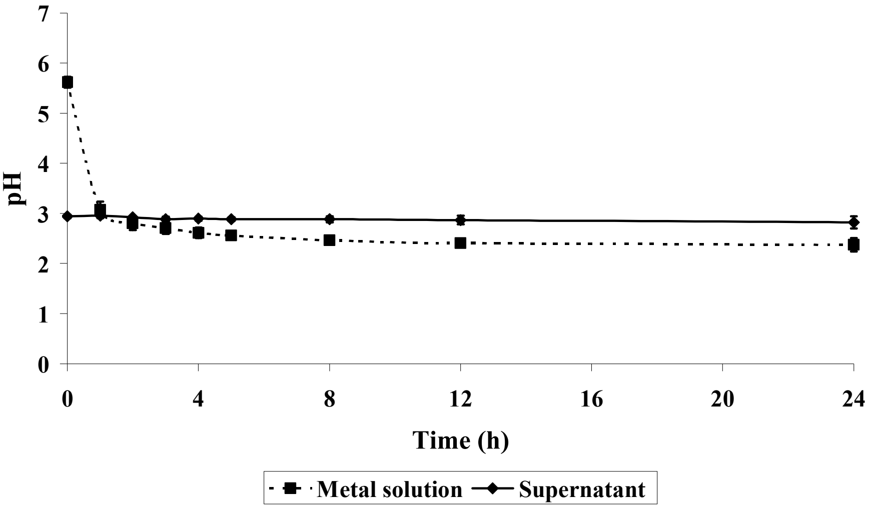


Figure 3.8 A typical pH profile from experiments with 250 mg/L Zn(II) in aqueous solution as the receiving water.

Figure 3.9 shows the sulphide transfer profile of an experiment with a 250 mg/L zinc(II) solution. There was a rapid decrease in sulphide concentration in the supernatant in the first 8 – 10 hours, after which equilibrium was reached. However, there was no corresponding rapid increase in sulphide concentration evident in the metal solution. This "missing" sulphide was assumed to now reside in the precipitated zinc(II) sulphide fraction of the system.

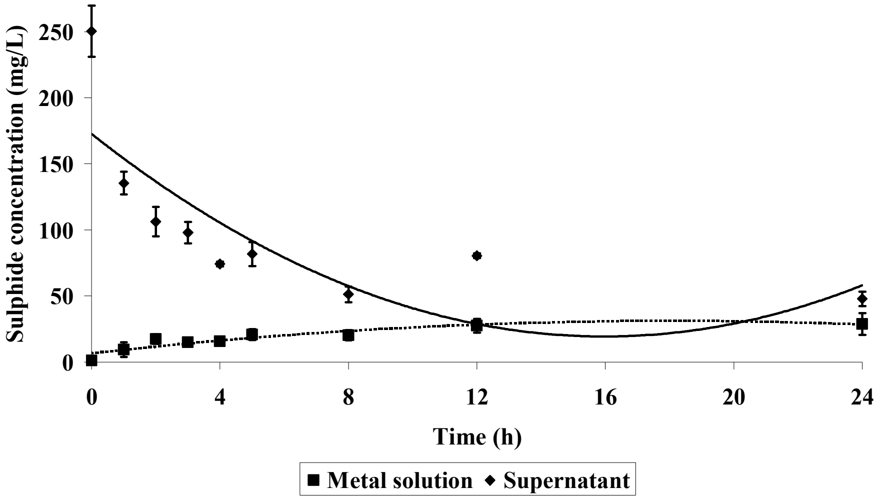


Figure 3.9 A sulphide profile from an experiment with 250 mg/L Zn(II) in aqueous solution as the receiving water.

After only 10 hours, less than 20 % of the zinc(II) remained in solution and a large amount of white precipitate was visible in the metal solution reservoir. This confirmed the assumption made regarding the sulphide removed from the supernatant and not measured in the metal solution. By comparing Figure 3.9 to Figure 3.10, it is apparent that 80 % of the metal precipitate was formed in the first 8 – 10 hours, when the sulphide levels dropped so rapidly.

After 24 hours, more than 90 % of the zinc(II) had been precipitated out of the solution (Figure 3.10). There were however, relatively large standard deviations between the triplicate samples, but as this corresponded with the distance each system was from the pump head, the slower flow rate further away from the pump head was thought to account for this.

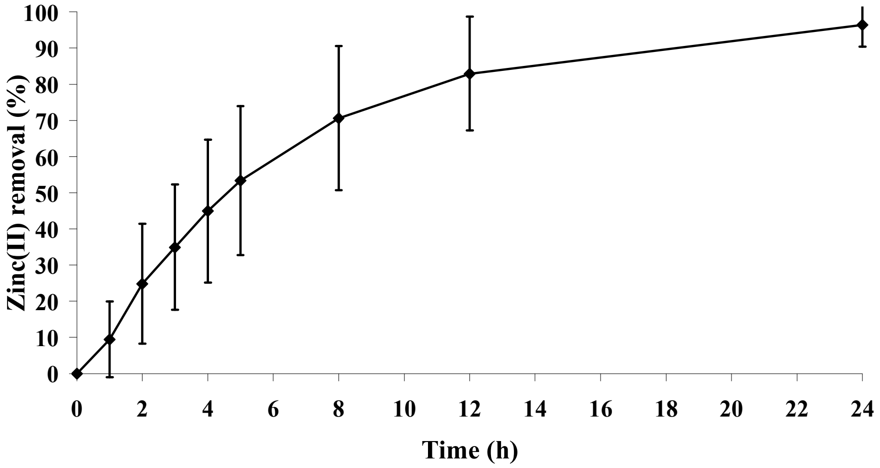


Figure 3.10 Removal of Zn(II) ions from an aqueous solution containing 250 mg/L Zn(II) over a 24 hour experiment.

The experiment was repeated using 250 mg/L copper(II) solution. The system pH was set in an identical fashion to the previous experiment with zinc(II), i.e. supernatant pH 3 and metal solution unchanged. In Figure 3.11, the sulphide profile shows almost no mass transfer of sulphide across the membrane. In the case of both the supernatant and the metal solution, the total sulphide concentration remained almost unchanged. Analysis of the copper solution showed that less than 10 % of the copper had precipitated before the formation of a precipitate layer on the silicone membrane halted any further transfer of sulphide.

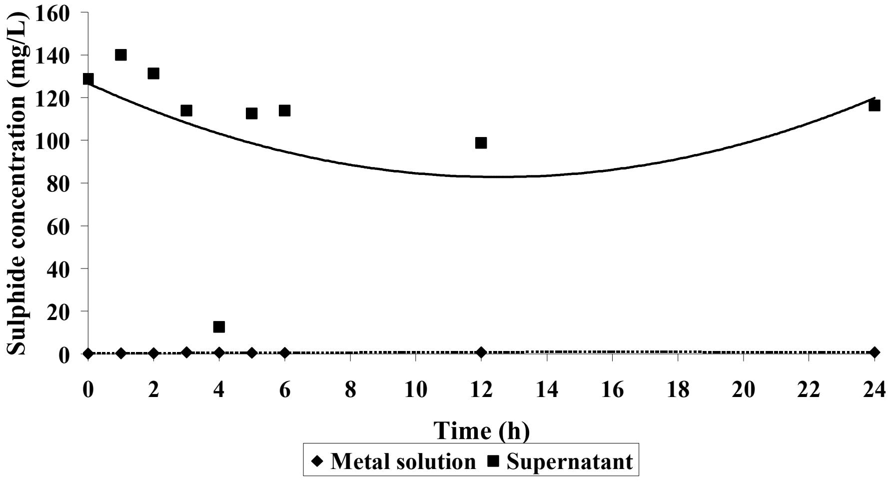


Figure 3.11 A typical sulphide profile from experiments with 250 mg/L Cu(II) in aqueous solution as the receiving water.

A similar result occurred when the experiment was repeated with a rhodium(III) solution (Figure 3.12). However, in this case, a larger amount of sulphide was able to penetrate the foulant layer and approximately 30 – 40 % of the metal was precipitated. The precipitate, however, was localized to the tubing surface and not released into the metal solution vessel.

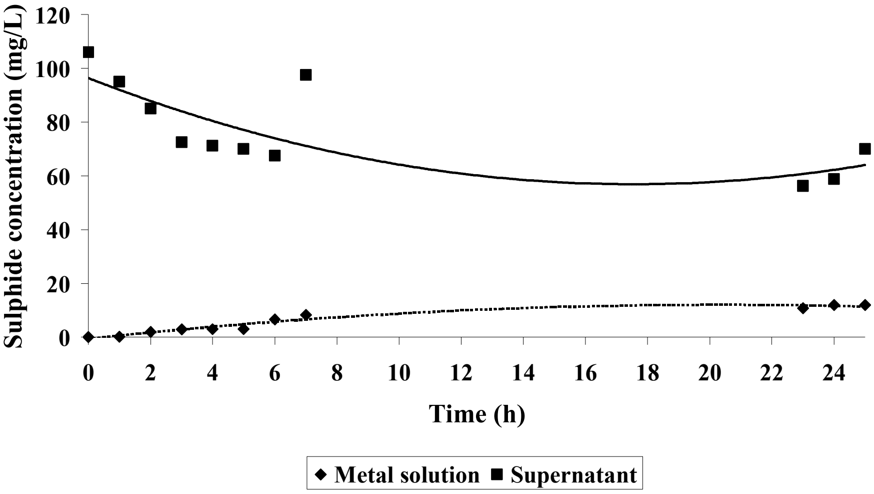


Figure 3.12 A typical sulphide profile from experiments with 60 mg/L Rh(III) in aqueous solution as the receiving water.

Several attempts to remove the precipitate layer from the membrane were made. The system design change, i.e. increasing the inner diameter of the membrane to promote turbulent flow and reduce fouling within the membrane had no impact on the formation of the foulant layer. The chemical methods applied were simple, cost-effective methods such as acid washing the tubing with both nitric and hydrochloric acids (both solutions 5 %) and short backwashing steps within the precipitation reaction itself. All attempts were unsuccessful. Vigorous and destructive mechanical cleaning of the membrane did result in removal of the precipitate layer. This removal method holds no advantage, as the destruction of a membrane after a relatively short period of use adds immense costs to the process operation.

3.5.3 DISCUSSION

Sulphide mass transfer was maximized in section 3.4.1, in this section; the principle of the SEMB was tested with a number of metal solutions. These experiments determined the applicability of the system as a metal recovery process.

The experiments with zinc(II) as the receiving metal solution, mirrored the experiments performed by Chuichulcherm *et al.* (2001), in which a rapid decrease in sulphide concentration in the supernatant along with a rapid decrease in the dissolved zinc concentration in the metal solution were noted. Chuichulcherm *et al.* (2001) concluded that a fast reaction occurred between the metal ions and the H_2S, similar to the rapid reaction shown in the present experiments. This rapid reaction seemed to enhance the transfer of H_2S from the supernatant into the metal solution by inducing an extremely steep H_2S concentration gradient. This gradient was maintained by the constant, rapid removal of sulphide on the metal solution side as a metal sulphide precipitate. A further enhancement of the gradient was the low pH of the supernatant, which increased the amount of non-dissociated H_2S, which increased the slope of the gradient even more. Stirring was thus not necessary as a means for enhancing the concentration gradient.

The removal of approximately 90 % of the zinc(II) in solution within 24 hours also corroborated the results obtained by Chuichulcherm *et al.* (2001), however, they did find that a thin layer of zinc sulphide precipitate attached to the membrane during the experiment, which may have decreased the transfer of H_2S by some degree. This was not found in the present study.

The decrease in the pH of the metal solution, from 5.6 to 2.3 was attributed to the release of hydrogen ions from the sulphide gas crossing the membrane, producing a weak sulphuric acid.

The experiments performed using copper(II) and rhodium(III) as the receiving metal solutions showed results vastly different to those obtained with zinc(II). The sulphide profiles showed almost no transfer of sulphide into the metal solution. This was due to the rapid formation of a layer of precipitate on the metal solution side of the membrane within the first hour of the experiment, made up of less than 10 % of the total copper(II) in solution and approximately 35 % of the rhodium(III) in solution. As the sulphide transferred and metal precipitation occurred, the precipitate adhered to the inside of the tubing, forming a layer impenetrable to any further gas transfer. No metal precipitation occurred subsequent to the formation of the layer. The amorphous copper film formed has been previously documented and has been investigated for its electrical and spectroscopic properties (Cruz-Vázquez *et al.*, 2001), where the CuS produced by reacting Na_2S with a copper(II) chelate produces an amorphous film supported on a substrate. It is possible that a similar phenomenon occurred with the rhodium sulphide species as they were similarly classified according to the HSAB theory and can thus be expected to behave similarly, but zinc(II) is also a borderline acid. This may suggest that copper and rhodium and zinc lie on opposite ends of the borderline acid spectrum, with zinc showing more hard acid and copper and rhodium showing more soft acid character.

Veeken *et al*. (2003) state that a major disadvantage of sulphide precipitation, in general, is the poor separation of metal sulphides from the water phase by means of solid-liquid separation processes such as sedimentation or filtration due to the production of colloidal metal sulphides. This may mean that depending on the metal targeted, its precipitation as a metal sulphide may not be feasible with the SEMB technology.

3.6 SULPHIDE-EXTRACTION MEMBRANE BIOREACTOR TRIAL: RECOVERY OF RHODIUM(III) FROM PRECIOUS METALS REFINERY WASTEWATER

As described in Chapter 2, the wastewater from which the rhodium is to be recovered is extremely hostile; low pH, high salinity and high ammonia levels all contribute to the recalcitrance of the wastewater. The high chloride concentration, in particular, may pose a problem if this in fact indicates the presence of chlorinated organic compounds. These compounds have been well documented regarding their ability to permeate silicone membranes. In fact, it is this quality that is exploited in a typical EMBR system. It is important to investigate the effects these compounds may have on the bioreactor if they are indeed present in the wastewater and capable of transferring into the biomedium.

3.6.1 MATERIALS AND METHODS

The same system set up was utilized as described in section 3.4.1. Wastewater was collected from a precious metals refinery over the course of a week to minimize the effect of small daily fluctuations. Alkalinity was measured according to Standard Methods (APHA *et al*., 1998). pH was measured using a Cyberscan 2500 pH meter (Eutech Instruments, Singapore) Spectroquant test kits (Merck, South Africa) were used to monitor sulphide (Spectroquant kit 1.14779) generation and chloride (Spectroquant kit 1.14897, analogous to method 4500-Cl- E (APHA *et al.*, 1998)) and ammonia (Spectroquant kit 1.14752, analogous to method 4500-NH3 G (APHA *et al.*, 1998)) concentrations. The utilization of sulphate in the bioreactor was monitored using a Spectroquant test kit (1.14791). All spectroquant test results were obtained using a Spectroquant Nova 60 photometer (South Africa). Atomic absorption spectrophotometric standard solutions were prepared from 1000 mg/L atomic absorption spectrophotometric standard solutions (Fluka, Switzerland) and diluted with deionized water until the desired concentration was achieved. All glassware used was prewashed in 5 % nitric acid and subsequently rinsed in deionized water to remove any possible interference by metal ions absorbed to the glassware surfaces. Analytical grade 3 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH) were used for pH adjustments.

Membrane bioreactor

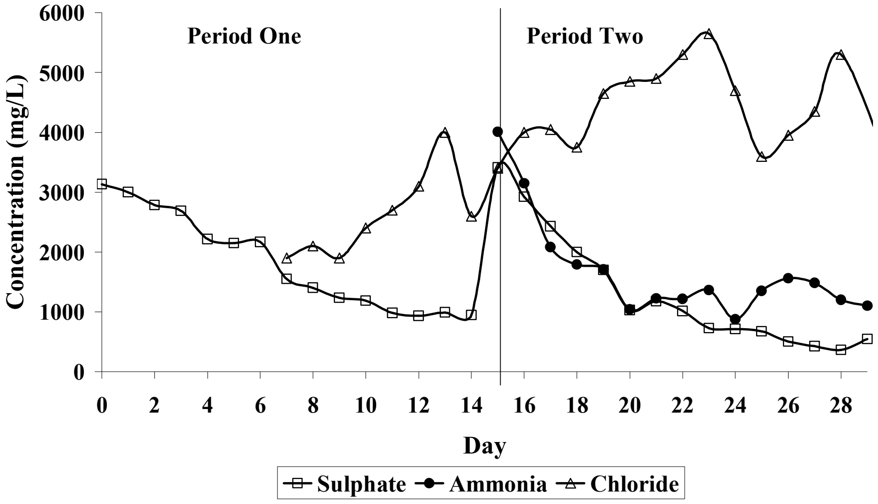
A 2 L aliquot of mixed liquor was removed from the bottom of the digester described earlier (3.4.1.2). This was centrifuged at 5000 rpm (Centrifuge 5403, Eppendorf, Germany) for 5 minutes to pellet the cells. The SRP cells were resuspended in 250 ml of double-strength modified Postgate medium, described in section 3.4.1. This formed the inoculum for the SEMB. The SEMB vessel, containing 1.75 L of double-strength modified Postgate medium, was inoculated on day 0. Each day, a 10 ml sample was removed from the SEMB. The SEMB was allowed to acclimate for four weeks before being challenged with the wastewater. After 14 and 28 days, 200 ml of fresh medium was added to the bioreactor to replace the volume removed for analysis. From the 10 ml sample extracted daily, sulphide production, alkalinity, pH, sulphate utilization, chloride concentration and ammonia concentration were monitored. After each sample was removed, the headspace of the bioreactor was sparged for 5 minutes with N_2 gas to retain an anaerobic environment and to prevent excessive pressure build-up inside the vessel. After four weeks, 2 L of wastewater was added to the receiving solution reservoir. This was pumped through the tubing submerged in the bioreactor at a flow rate of 20 ml/min for two weeks. A 5 ml sample was removed from the wastewater each day in order to monitor the movement of sulphide across the membrane.

Precipitate analysis

After the wastewater had circulated for two weeks the system was shut down and the wastewater was filtered through dried preweighed 0.45 µm pore size cellulose acetate filters (Whatman, England) to separate the precipitated component. The filters were dried overnight at 100 ºC and reweighed (this process was continued until no significant weight change was noted) to determine the mass of the precipitate. Two 1 g samples of the dried precipitate were vigorously digested with hot nitric acid to enable the determination of the total metal content (APHA *et al.*, 1998) via atomic absorption spectrophotemetry (GBC 909 AA, Avanta, Australia).

3.6.2 RESULTS

The initial sulphate concentration in the biomedium was approximately 3100 mg/L (Figure 3.13A), this dropped to less than 1000 mg/L after the first two weeks (day 15). The pattern was repeated in the second two-week period, when an initial concentration of 3600 mg/L was reduced to less than 1000 mg/L. In the graph, it can also be seen that chloride showed a production trend and ammonia a utilization trend. Free chloride ions were released because of the metabolism of the nitrogen source, NH_4Cl, present in the medium. In the same figure, the utilization of ammonia as a nitrogen source can be seen. The total sulphide concentration remained at approximately 500 mg/L for the duration of the six-week experiment (Figure 3.13B). This level was probably sustained by the daily N_2-sparging of the bioreactor headspace, allowing a constant movement of gas from the liquid phase to the gas phase and into the zinc acetate trap. Alkalinity is a measure of the buffering capacity of a solution and as this buffering is usually performed by a bicarbonate system, the breakdown products of complex carbon sources add to this pool of bicarbonate/carbonate. As indicated in Figure 3.13B, the alkalinity never reached a plateau, meaning that the carbon source was never exhausted. The pH of the biomedium closely followed the trend exhibited by the alkalinity. This is due to the increase in hydrogen-ion-absorbing capacity as the alkalinity increases. This forces the pH to rise concurrently with the alkalinity.



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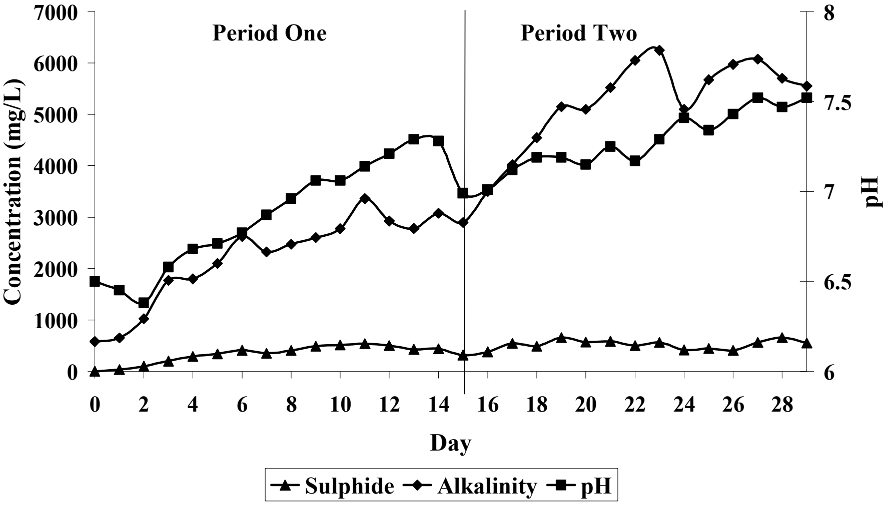

B

Figure 3.13 Results of daily monitoring of bioreactor for periods one and two.

In the third period (Figure 3.14), wastewater was pumped through the silicone tubing at a flow rate of 20 ml/min. All parameters previously mentioned were monitored. Within the first 48 hours, a precipitate had collected at the bottom of the metal solution reservoir and a layer of precipitate had formed on the inside of the silicone tubing. The experiment was continued, however, to determine whether continuous turbulent flow over the precipitate would result in the precipitate sloughing off at any stage. This was not the case. The precipitate remained in place and no further increase in the quantity of free precipitate was noted.

Sulphate reduction was not as rapid during the third period; on day 44 more than 2000 mg/L remained unreduced. However, despite the higher final concentration of sulphate, the sulphide level remained relatively constant. This may be an indication that sulphide was no longer able to permeate from the biomedium into the wastewater due to the membrane fouling, creating a build-up within the bioreactor. The reduction in sulphate utilization may be a response by the SRP to the possibly toxic effects of a further increase in sulphide levels**.** The ammonia and chloride levels showed a continuation of the pattern established in periods one and two. There was no indication that movement of molecules in any direction across the membrane was affecting the biomedium ion levels. This again, may have been due to the precipitate build-up. The alkalinity and pH in the biomedium maintained a constant increase throughout period three and seemed unaffected by any movement of molecules through the membrane from the wastewater.

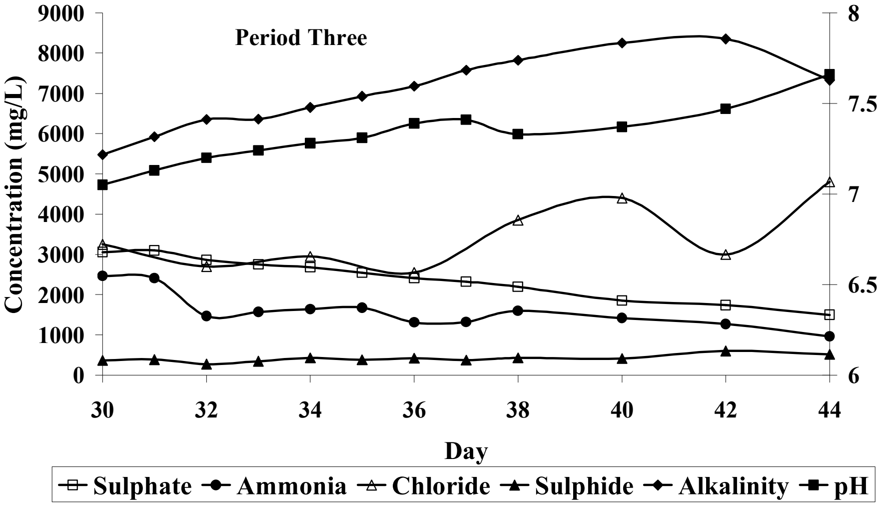

Figure 3.14 Results of daily monitoring of bioreactor for period three.

In Figure 3.15, the results from the monitoring of the wastewater are shown. Here it becomes obvious that little or no movement of ions through the silicone tubing took place. Both the ammonia and chloride levels remained at stable high levels and the pH showed no substantial change throughout the two weeks.

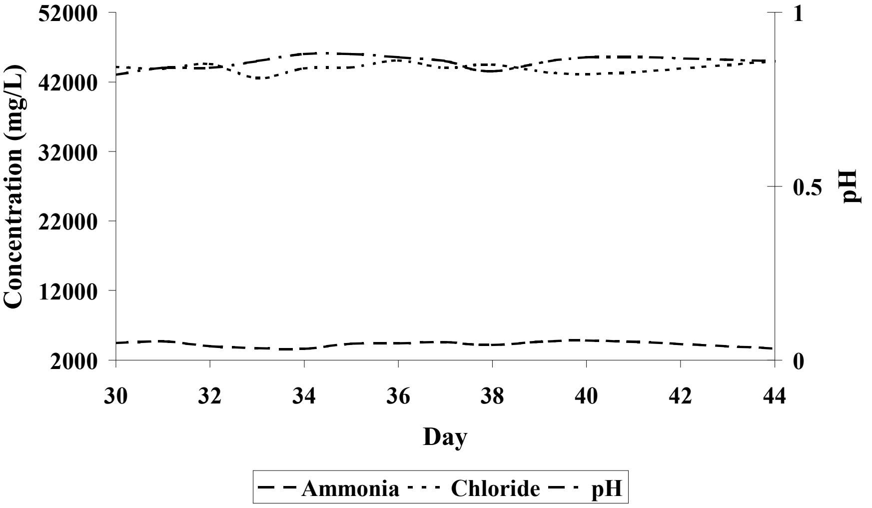

Figure 3.15 Results of daily monitoring of wastewater in period three.

The sulphide profile (Figure 3.16) shows that during the first 48 hours after introduction of the wastewater (days 30-32), sulphide did pass through the tubing and initiate metal precipitation. This can be inferred from the evidence showing that no sulphide was present in the wastewater solution over that period, but after that it remained at a constant level of below 100 mg/L. The sulphide content of the bioreactor did not show any considerable decrease over the period except during the first 48 hours. An increase was noted on day 41, but this may be a result of the sample being taken at a different time, allowing a higher build-up of sulphide before N_2-sparging.

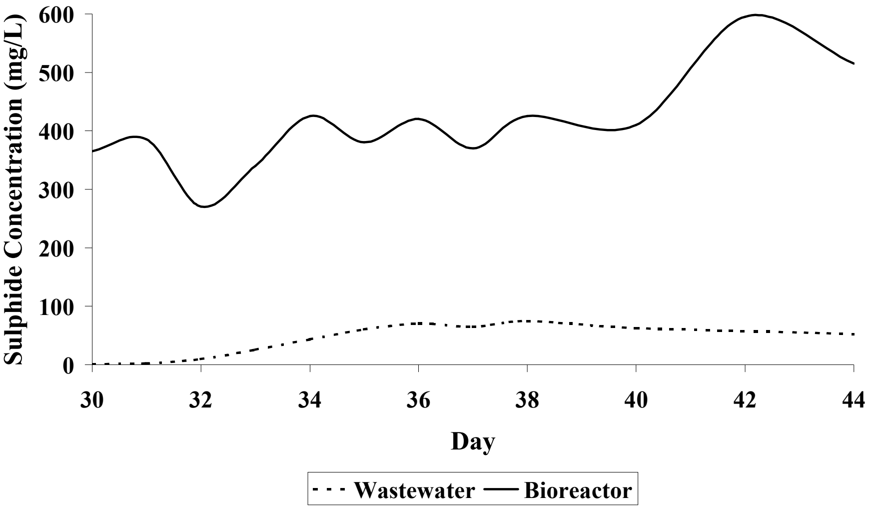

Figure 3.16 A sulphide profile of the SEMB system in period three.

The precipitate generated in the first 48 hours after exposing the wastewater to the sulphide generated by the bioreactor was analysed to determine its precious metal component. This was compared to the aqueous components before treatment and after filtration of the precipitate. Figure 3.17 describes the total metal present in each of these fractions. The graph indicates that the largest mass of precious metal present in the precipitate was rhodium. This was expected, as rhodium was present in the highest concentration in the wastewater. Gold and palladium, as expected, were present in trace amounts only, as these metals are extracted much earlier in the refining process (Figure 2.2).

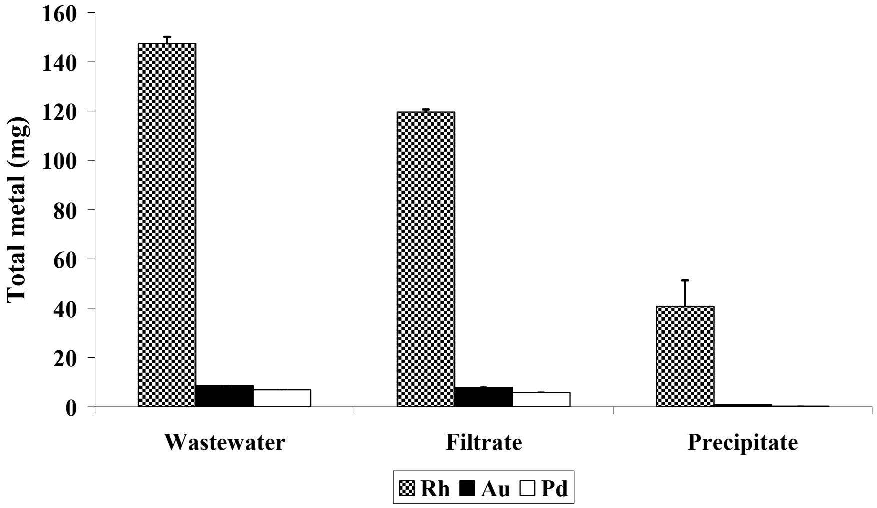

Figure 3.17 A comparison of the precious metal makeup of the effluent fractions resulting from the bench trial.

Table 3.2 shows the percentage removal of the three metals measured in the precipitate. This shows that despite the largest amount of metal in the precipitate being rhodium, the actual percentage removals for rhodium and palladium are similar (18.87% and 15.80%, respectively), indicating no significant preference for one metal over the other. Less than 20% of the rhodium present in the wastewater was precipitated in the first 48 hours. Table 3.2 also shows that of the 11.165 g of precipitate, rhodium, gold and palladium did not account for even 1%. This indicates that there is something present in the wastewater that precipitates preferentially when in contact with sulphide ions.

Table 3.2 Total metal content of the separated fractions resulting from the bench trial.

Wastewater component	**Total metal content (mg ± S.D.), percentage of precipitate and percentage removal (%)**								
	Rhodium			Gold			Palladium		
	Total metal	Precipitate	Removal	Total metal	Precipitate	Removal	Total metal	Precipitate	Removal
Wastewater	147.35 ±2.76			8.56 ±0.18			6.96 ±0.15		
Filtrate	119.54 ±0.18			7.77 ±0.21			5.86 ±0.11		
Precipitate [a]	40.77 ±10.50	0.37	18.87	0.88[b]	> 0.01	9.23[b]	0.27[b]	> 0.01	15.80[b]

[a] Total mass of precipitate = 11.165 g [b] Lower limit of instrument detection, large variation between samples.

3.6.3 DISCUSSION

The bioreactor showed similar production and utilization cycles during the initial two-week periods in which it operated. Sulphate reduction and sulphide generation were constant, proving that the SRP present within the bioreactor were actively respiring. The ammonia and chloride ion concentrations were monitored to determine whether compounds were able to pass from the wastewater into the bioreactor medium. These ions were chosen due to their high concentration in the wastewater and the capacity for chlorinated organic compounds to permeate the silicone membrane, and since the organic content of the wastewater was not known, this was monitored as a precaution.

During the third two-week period, wastewater was constantly circulated through the membrane. Within the first 48 hours, a precipitate had formed, both on the membrane and in the metal solution reservoir. The precipitate layer on the membrane drastically slowed the transfer of H_2S from the bioreactor to the metal solution, causing a sulphide build-up within the bioreactor. It was thought that this build-up was responsible for the slower reduction of sulphate by the SRPs during this period. It was also noted during this period that no ammonia or chloride ions were transferred from the wastewater into the bioreactor. The sulphide concentration within the metal solution remained constant after the initial 48 hours. This maintenance of a sulphide concentration was unexpected as it was thought that all sulphide being exposed to the wastewater would be removed as part of the precipitate. It was hypothesized that after 48 hours had elapsed only a very small amount of metal ions of a species amenable to precipitation were present. Thus, no further significant decrease in sulphide levels was possible as a result of precipitation.

Analysis of the precipitate after the conclusion of the experiment showed that the largest precious metal precipitate portion was composed of rhodium sulphide precipitates. Only palladium and gold were found in any other significant proportion when measuring the precious metal contribution to the precipitate. However, these contributions totalled less than 1 % of the total precipitate mass. It can only be assumed that the remaining 99 % was composed of other non-metallic or metallic ions present in the wastewater. This implied an extreme tendency to non-specific precipitation of all precipitable ions in solution.

3.7 SUMMARY AND CONCLUSIONS

Efficient transfer of sulphide gas across the silicone membrane was found to be highly dependent on the pH of the system when using water as a receiving solution. An initial experiment run without pH adjustment showed a baseline mass transfer rate of 1.47×10^{-6} m/s. Maximum transfer was achieved by adjusting the pH of the biogenic sulphide source (the supernatant) from a pH of 7.8 to approximately 3. This gas transfer was best monitored when the receiving solution pH matched that of the supernatant, i.e. pH 3. These adjustments resulted in a threefold increase in sulphide mass transfer, to 3.25×10^{-6} m/s. Agitations of the membrane-containing vessel served to increase the mass transfer tenfold compared to the initial experiment. Under these circumstances, the overall mass transfer coefficient was found to be 1.04×10^{-5} m/s. However, although pH adjustment and agitation made a significant difference to the mass transfer of sulphide through the membrane, it may not be necessary. If the concentration gradient is maintained at levels steep enough to drive the gas through i.e. if a high initial sulphide concentration is present, the movement will occur spontaneously, with the concomitant drop in pH increasing the amount of dissolved H_2S, thus maintaining the gradient (and the driving force). Chuichulcherm *et al.* (2001) showed evidence for this in their experiment with zinc, where neither the pH of the supernatant nor the metal solution was adjusted and yet greater than 90 % removal was achieved.

The experiments using metal solutions were all pH-adjusted where possible, i.e. it was impossible to adjust the metal solutions without initiating spontaneous precipitation of the metal, but the supernatant was adjusted to a pH of 3 each time. The experiments with zinc(II) showed model results, a sharp drop in sulphide concentration in the supernatant and an equally sharp decline in the metal concentration in the metal solution. Removal of more than 90 % of the zinc was achieved within 24 hours. This result correlates well with data published by Chuichulcherm *et al.* (2001).

The copper experiments, however, did not show positive results. Within the first hour after initiation of the experiment, a layer of precipitate had formed that seemed to greatly impede any further transfer of sulphide. In that first hour, less than 10 % of the available copper was precipitated and after 24 hours, the result had not changed.

The experiments with rhodium solution showed similar results to the copper experiments. Within a few hours of initiation of the experiment, a layer of precipitate had effectively blocked any further sulphide transfer. There was, however, a greater removal of rhodium than there was of copper. Between 30 and 40 % of the available rhodium was precipitated over the 24-hour period. This suggests that the reaction between dissolved rhodium ions and sulphide ions is slower than that occurring between the copper ions and sulphide.

Visual observation of the three precipitates formed indicated that the structure of the precipitate may be an indication of whether or not a metal sulphide would adhere to the membrane. The zinc sulphide precipitate exhibited a crystalline solid structure (similar to an insoluble salt), whereas both the copper and rhodium sulphide precipitates exhibited an amorphous structure with very low settlability. Attempts were made to remove the rhodium precipitate using both chemical and physical methods.

Acid washing of the intact membrane as well as backflushing with water did not remove the layer. Only after dismantling and cutting open the membrane could the precipitate be removed by vigorous scrubbing. This result is extremely detrimental to the overall process and if this were the only method capable of recovering the rhodium precipitate from the membrane, the membrane would effectively become single use only, greatly increase running costs.

When run as a complete process, i.e. an actively growing bioreactor coupled to the membrane system, the wastewater seemed to have no effect on the SRP. The bioreactor functioned optimally for six weeks and no counter transfer of indicator ions (chloride and ammonia) was measured. Only 24 hours after the wastewater was introduced into the membrane system, a large amount of precipitate had formed and the membrane seemed to be fouled as no further sulphide transfer took place. Analysis of the precipitate showed that less than 1 % of the 11.165 g of the dried precipitate was made up of precious metals (rhodium, gold and palladium). The remainder would most likely include some base metal precipitates and some elemental sulphur.

Despite the foulant metal drawback, the SEMB, when used to treat the correct metal, compares favourably to other small-footprint SRP technologies tested using single metal solutions. El Bayoumy *et al.* (1999) investigated an upflow anaerobic fixed-film reactor with SRP to remove zinc ions. At an initial concentration of 150 mg/L, 100 % removal was achieved. However, at 200 mg/L zinc, the removal dropped to less than 80 %. This was thought to be due to metal toxicity. This is something from which the SEMB does not suffer, as the SRP are maintained remote from the wastewater. Thus, at metal ion levels higher than that of El Bayoumy *et al.* (1999), greater than 90 % of the zinc ions were removed.

However, despite the excellent and reproducible results obtained from the experiments with zinc(II), the SEMB does not seem to be suitable as a process for the selective recovery of rhodium(III) from wastewater. The results have shown a distinct lack of specificity and a tendency for components within the wastewater to form a foulant layer that resists the transfer of H_2S into the wastewater. Possibly, pre-treatment of the wastewater may render it more amenable to metal recovery via the SEMB, but this would increase the cost and complexity of the recovery system. In view of the negative results obtained from this study, other low-cost treatment technologies will be investigated in order to find a process suitable for the recovery of rhodium(III) ions from refinery wastewaters.

CHAPTER 4

A FLUIDIZED SAND BED REACTOR FOR THE RECOVERY OF RHODIUM(III) FROM PRECIOUS METAL REFINERY WASTEWATER

4.1 INTRODUCTION

Chemical precipitation is the simplest and cheapest means of removing most heavy metals from solution and as such, is the most widely used treatment process in industry (Veeken and Rulkens, 2003; Cowan, 1998). Precipitation is generally achieved by increasing the pH of the wastewater, thereby precipitating the metal in an insoluble form, usually its hydroxide (Eccles, 1999). However, this treatment often requires large land investments for treatment and settling tanks, as well as sludge dewatering and disposal facilities.

A great deal of interest in alternatives to the basic precipitation system has been shown and has sparked investigations into the substitution of a single fluidized bed reactor for both the treatment and settling tanks required for the conventional process (Zhou *et al*., 1999; Nielsen *et al*., 1997; Aktor, 1994). A major disadvantage of conventional continuous-flow chemical precipitation processes is that they generally require a number of steps, each requiring a separate tank environment. Added to the space disadvantage, dewatering and/or solidification are often necessary before disposal can be effected. The combination of these separate processes (reaction and settling) into a single reactor configuration (fluidized bed) would greatly enhance the attraction of the system as a metal recovery process. If the processes can be combined in a way that removes the necessity for dewatering or solidification, all the better.

Research undertaken at the Hong Kong University of Science and Technology has resulted in the development of a single-step space-saving precipitation process for the removal of heavy metals by chemical precipitation (Sun and Huang, 2002). ‘Nucleated precipitation’ or ‘pellet crystallization’ allows for soluble metal ions to become coated or plated onto sand particles present in a fluidized sand bed. This technology has been implemented in a limited number of cases, and the results show great potential for the removal of metal ions from wastewater solutions. Zhou *et al*. used this technique in 1999, based on the induction of nucleated precipitation of metal ions on to sand particles present in a fluidized bed reactor to recover copper, nickel and zinc ions. The induction method used was the addition of carbonate ions (in the form of sodium carbonate solution) at a molar ratio of 2/1 [CO_3]/[metal]. The results obtained showed that pH had the greatest effect on removal efficiency and the optimum pH for precipitation was approximately 9.0 – 9.1. The synthetic wastewater used contained copper, nickel and zinc ions, and at the optimum pH levels, greater than 90 % removal was achieved. Throughout their experiments, metal removal was only measured as nucleated precipitation. Any discrete precipitation that occurred was not regarded as metal removal.

The design of a fluidized or expanded bed reactor is represented in Figure 4.1. Wastewater is passed from the base of the reactor, up through a bed of particulate media. The velocity of this waste stream causes the fluidization or expansion of the bed by countering the natural tendency of the media to settle into a packed bed (King *et al*., 1998; Banks, 1997). This movement of the media maximizes the surface area available for microbial attachment and for particle adsorption (Volesky, 1990).

Of critical importance is the density of the particulate media, as this parameter influences the process energy requirements and determines the manner in which the fluidization force is applied. In an expanded bed this force is the upflow velocity of the liquid, where the flow is maintained at a velocity approximately equal to the sedimentation velocity of the particles. This grants the particles only limited movement relative to one another and the void volume of the reactor is larger than that of a packed bed of the same material. In a fluidized bed, a greater force is applied, resulting in the unrestricted movement of particles relative to one another, creating random motion within a defined volume (Banks, 1997).

The constant motion of the particulate media within the wastewater implies a twofold advantage, one being the efficient mass transfer across the particulate surface that minimizes the potential for localized concentration gradients. The second advantage is the prevention of clogging and channelling within the reactor, allowing for the treatment of wastewater streams containing suspended material (Banks, 1997). Other advantages of the fluidized bed reactor for the treatment of wastewater include:

- Proven operation in aerobic, anaerobic and facultative anaerobic modes (Forster, 1985).
- High upright volume maximises space utilisation.
- Little or no maintenance.
- No plugging due to solids build-up or gas mobilisation of sludge.
- Documented ability to treat high BOD/COD loadings.
- Resistant to abrupt changes in flow and waste concentration.
- May require only minimal nutrient addition (King *et al.*, 1998).
- Maintains a high biomass concentration without need for solids recycle (Forster, 1985).

However, due to the fluidization, a larger volume is required in the column and thus space efficiencies are lower than in a packed bed reactor system (Volesky, 1990).

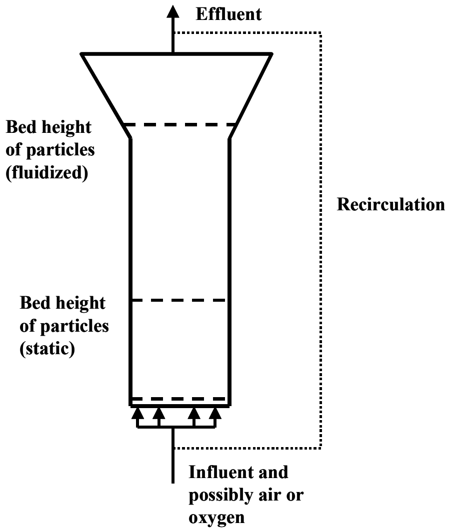

Figure 4.1 Design of a standard fluidized bed reactor (Banks, 1997).

4.2 HYPOTHESIS

By addition of the optimum sodium carbonate solution concentration to the PMR wastewater, nucleated precipitation of rhodium ions onto sand particle present in a fluidized bed reactor will occur.

4.3 AIMS AND OBJECTIVES

The overall aim was to investigate the application of nucleated precipitation in a fluidized sand bed for the recovery of rhodium(III) from process wastewaters. In order to achieve this, the following objectives were set:

- Determine the optimum carbonate/metal ratio for nucleated precipitation.
- Determine the extent to which simple electrostatic adsorption onto sand particles contribute to removal of rhodium.
- Conduct a bench-scale trial using the wastewater described in Chapter 2.

4.4 BATCH STUDIES TO DETERMINE THE SUITABILITY OF SAND GRAINS AS AN ADSORBENT FOR RHODIUM PRECIPITATES

The first aim of this study was to determine the ratio of carbonate/metal ions that produced sufficient precipitation of rhodium to induce nucleation onto the sand grains. The second aim was to determine whether any purely electrostatic adsorptive effects would aid in the induction of nucleation onto the sand grains.

4.4.1 MATERIALS AND METHODS

All reagents were of laboratory grade. All glassware was acid washed in 5 % HNO_3 and rinsed in distilled water before use. Rhodium metal solutions were made up by diluting a 1000 mg/L rhodium atomic absorption standard solution (Fluka, Switzerland) with distilled water until the desired concentration was reached. Graded silica media of nominal diameter 0.95 mm (S & E Silica, South Africa) was used as a particulate media. Before use, the sand was acid-washed in 5 % HNO_3, rinsed with tap water and finally soaked in distilled water for 1 hour.

Determination of the optimum carbonate/metal ratio for precipitation

Five sodium carbonate (Na_2CO_3) solutions were made up, the first at equal molarity to a 20 mg/L rhodium solution. The subsequent four were at ratios of 1.5/1, 2/1, 4/1 and 6/1 respectively. Three replicates of 9.8 ml of each carbonate solution were dispensed into test tubes. The experiment was initiated upon addition of 200 µl of a 1000 mg/L rhodium standard solution (resulting in a 20 mg/L solution). Two blanks were prepared and ran concurrent to the experimental test tubes. The first contained only a sodium carbonate solution, the second only a metal solution. The test tubes were agitated for three hours (Labcon shaker, South Africa), at which time it was estimated that equilibrium had been reached. The samples were then filtered through 0.45 µm pore size cellulose acetate filters (Whatman, England) and assayed for soluble rhodium concentration using atomic absorption spectrophotometry (GBC 909 AA, Avanta, Australia).

Determination of the optimum sand concentration and time taken to reach equilibrium

Three replicates of each chosen sand concentration (100 g/L, 200 g/L, 250 g/L, 300 g/L, 350 g/l, 400 g/L) were placed in 100 ml conical flasks. 50 ml aliquots of a 60 mg/L rhodium solution were added and the flasks were agitated at 150 rpm for three hours. At regular intervals (30 min, 90 min, 120 min, 180 min and 240 min) a 3 ml sample was removed from each flask, filtered through a 0.45 µm pore size cellulose acetate filter and assayed for rhodium concentration by atomic absorption spectrophotometry.

Determination of the adsorptive capacity of sand grains

Two adsorption isotherms were produced, the first to determine whether pH adjustment affected the electrostatic adsorption of rhodium to the sand, and the second to determine if temperature affected adsorption. The subsequent addition method (SAM) for adsorption isotherm construction was used (Pagnanelli *et al*., 2000). Aliquots of 50 ml of distilled water adjusted to relevant pH were added to nine 100 ml conical flasks, three at pH 1, three at pH 2, and three at pH 3. 200 g of sand (Zhou *et* *al*., 1999) was added to two flasks at each pH, the third served as a control. All flasks were agitated at 200 rpm on a bench top shaker. The experiment was initiated by the addition of 2 ml of 1000 mg/L rhodium solution, followed by pH correction with either 1 M NaOH or 1 M HCl. After an experimentally defined equilibration time (90 minutes, from experiment to determine time to reach equilibrium), a 3 ml sample was taken, a second aliquot of 2 ml of 1000 mg/L rhodium solution was added, and a second pH correction was made. This was continued for five additions. All samples were filtered through a 0.45 µm pore size cellulose acetate filter and assayed for rhodium concentration by atomic absorption spectrophotometry.

4.4.2 RESULTS

Determination of the optimum carbonate/metal ratio for precipitation

None of the tested molar carbonate/metal ratios precipitated more than 20 % of the soluble rhodium. The highest achieved was 18.75 % at a ratio of 2/1, followed by 18.72 % at 1.5/1. However, if the standard deviations are considered, there was no significant difference between the first four ratios. The highest ratio, 6/1, precipitated the lowest amount of rhodium, less than 15 %. Figure 4.2 indicates that a ratio of between 1/1 and 4/1 was optimal for precipitation.

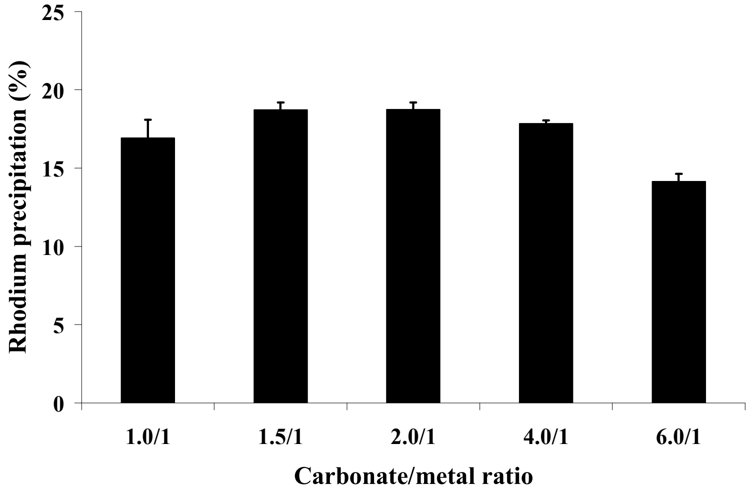

Figure 4.2 Bar graph indicating the optimum carbonate/metal ratio for precipitation.

Determination of the optimum biomass concentration and time to reach equilibrium for removal of rhodium

Figure 4.3 does not show a stable adsorption pattern for rhodium onto the sand grains. But at all concentrations a peak existed at 90 minutes. This peak was highest for the 200, 250 and 400 g/L concentrations. However, the 400 g/L concentration showed highly erratic results after 90 minutes, dropping down to below 2 % removal at 180 minutes and rising to a final percentage removal of 10.5 % removal at 240 minutes. Both the 200 and the 250 g/L concentrations remained far more stable subsequent to the 90-minute sample. These concentrations dropped from a 12 % removal at 90 minutes to an 8 % removal for the 200 g/L and a 7 % removal for the 250 g/L concentration. It was also determined from Figure 4.3 that the time to equilibrium would be approximately 90 minutes, as it was at this time that the sand concentrations exhibited their highest percentage removals.

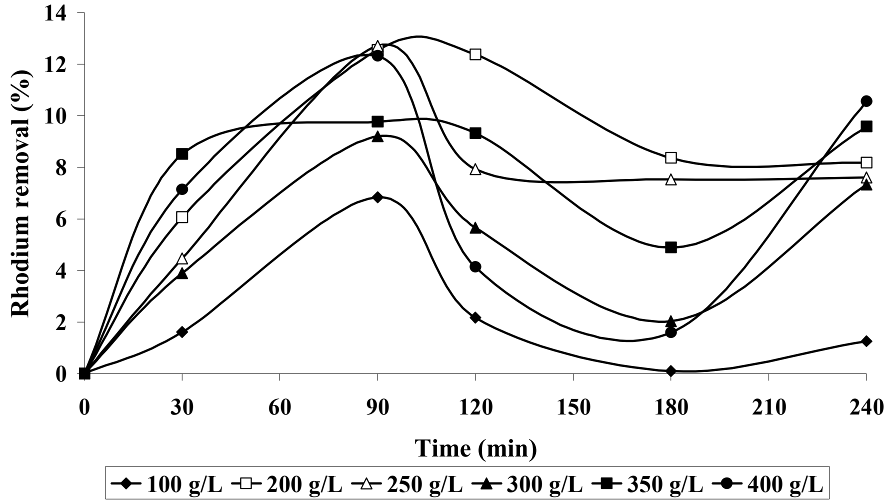

Figure 4.3 Adsorption kinetics of rhodium ions interacting with sand grains (SD not shown, generally < 8 %).

Determination of the adsorptive capacity of sand grains by construction of adsorption isotherms

Figure 4.4 allows for a comparison between the experimental flasks and the control (blank) flasks to be made. This comparison showed that, when considering the standard deviations between experimental and control, there was no significant difference between the two. This lack of sample deviation from the control implied that no adsorption took place and any decrease in soluble rhodium could be attributed to spontaneous precipitation or adsorption to the glassware surface. It can be seen from these results that at the lowest pH, i.e. 1, the rhodium ions were most soluble.

This pH exhibited the highest equilibrium concentration at each addition step, meaning that the least spontaneous precipitation took place at this pH.

Figure 4.5 shows a similar trend to that exhibited in Figure 4.4. There was no significant difference between the experimental and control flasks. Thus, no adsorption took place. All that can be suggested from Figure 4.5 is that rhodium ions are generally more soluble at lower temperatures. Due to the lack of sample deviation from the control experiments, no adsorption isotherms could be constructed from the data.

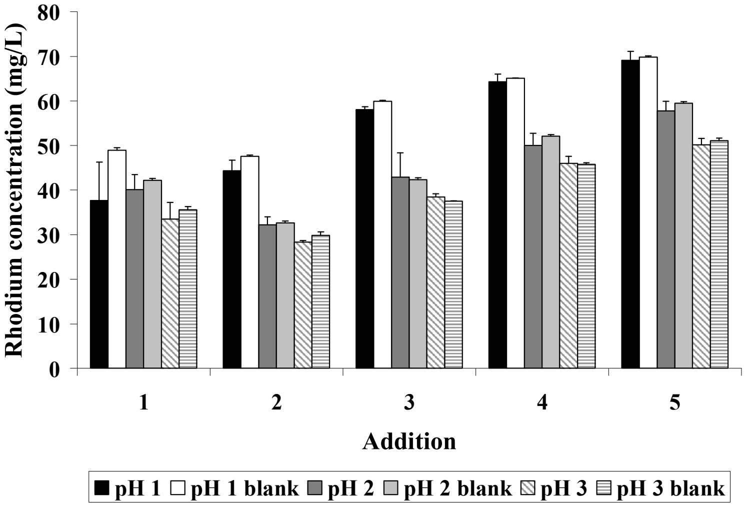

Figure 4.4 Bar chart illustrating the data obtained for the pH isotherm.

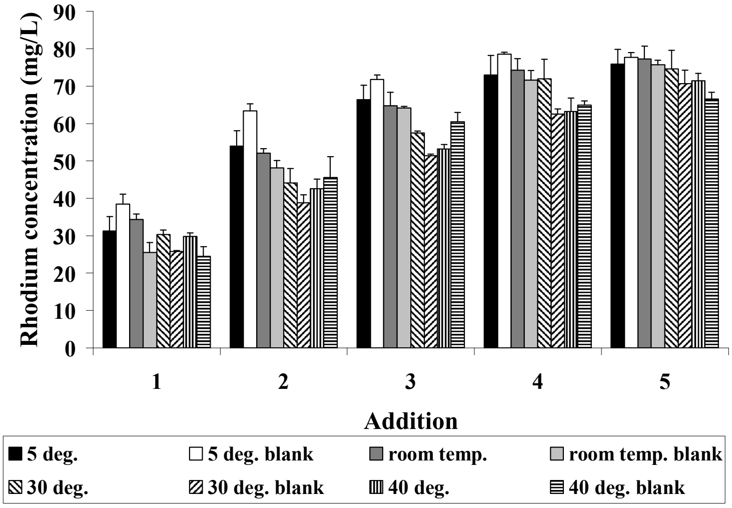

Figure 4.5 Bar chart illustrating the data obtained for the temperature isotherm.

4.4.3 DISCUSSION

In determining the carbonate/metal ratio optimal for precipitation, no significant difference was noted between the ratios ranging from 1/1 to 4/1. All were capable of precipitating between 16 and 19 % of the soluble rhodium. At the higher ratio of 6/1, less than 15 % was precipitated. It was not understood why a higher ratio, which would seem to speed up precipitation, did not show this expected trend. However, Zhou *et al.* (1999) also used a ratio of 2/1 as they showed that a ratio higher than this induced such rapid discrete precipitation in the fluidized bed that it excluded any chance for nucleated precipitation to occur on the sand grains.

The experiment to determine the equilibrium time and optimum sand concentration did not show clearly conclusive results. In terms of the time taken to reach equilibrium, no clear equilibrium was reached at any sand concentration, but the adsorption peak at 90 minutes for each concentration was used as an indication of an adsorption threshold and was therefore used in the isotherm construction experiments. There was no discernible pattern of increase in adsorption efficiency along with the increase in sand concentration. A concentration of 200 g/L was selected as optimal due to the most stable adsorption curve being produced by that concentration. This selection was in agreement with the sand concentration used by Zhou *et al*. (1999).

An adsorption isotherm is designed to facilitate a comparison between adsorbent materials based on specific metal ion uptake (mg metal adsorbed per g of adsorbent material). However, if a comparison is not necessary, calculation of the specific uptake is still valuable as it gives an indication of the adsorptive capacity of the material. It is also a simple method of determining a number of parameters involved in the optimization of that metal uptake, i.e. optimum temperature, pH, biomass concentration, etc. In this case however, the results revealed none of this information, and suggested that no adsorption affinity exists between the rhodium ions and the sand particles. This shows conclusively that no simple electrostatic adsorption effects exist that may aid in the nucleation of rhodium and rhodium precipitates onto the sand surfaces.

Despite showing that adsorption could play no role in the nucleated precipitation of rhodium onto the sand particles, the possibility that precipitation alone was sufficient to initiate the nucleation was sufficient motivation to continue the study and conduct fluidized bed reactor experiments with the wastewater.

4.5 BENCH TRIAL OF FLUIDIZED SAND BED REACTOR

4.5.1 MATERIALS AND METHODS

The fluidized sand bed was constructed as illustrated in Figure 4.6. The total height of the fluidized bed was 30 cm, with a diameter of 3.7 cm. The height of the static sand bed was approximately 14 cm. The minimum flow rate necessary to fluidize the sand was 1020 ml/min (Watson-Marlow 504S, England) and this flow rate was used for all experiments. All bench trials were run using rhodium-laden wastewater and a sodium carbonate solution at a carbonate/metal ratio of 2/1. After the initial mixing cycle, the wastewater and carbonate solution was recycled until a retention time of 7.1 minutes was reached. Both the soluble and total rhodium concentrations were determined after each experiment. The soluble concentration was determined as mentioned previously, using atomic absorption spectrophotometry. The total concentration was determined by acid digestion of a well-mixed sample (APHA *et al*., 1998), followed by the sample treatment as for the soluble metal determination.

4.5.2 RESULTS

An initial experiment was performed, in which 1 L of wastewater was mixed with 1 L of (2/1) sodium carbonate solution and passed through the fluidized bed until a retention time of 7.1 minutes was reached. This process was repeated three times to determine the reproducibility of the process. Between each replicate, the sand was changed and the column was acid washed and rinsed with distilled water until the pH of the water rose to above 6.

A second experiment was designed to determine the number of times a single 200 g mass of sand could be reused. In this case, there was no acid washing or rinsing between each wastewater addition. In all 5 L of wastewater was treated (i.e. 10 L of liquid).

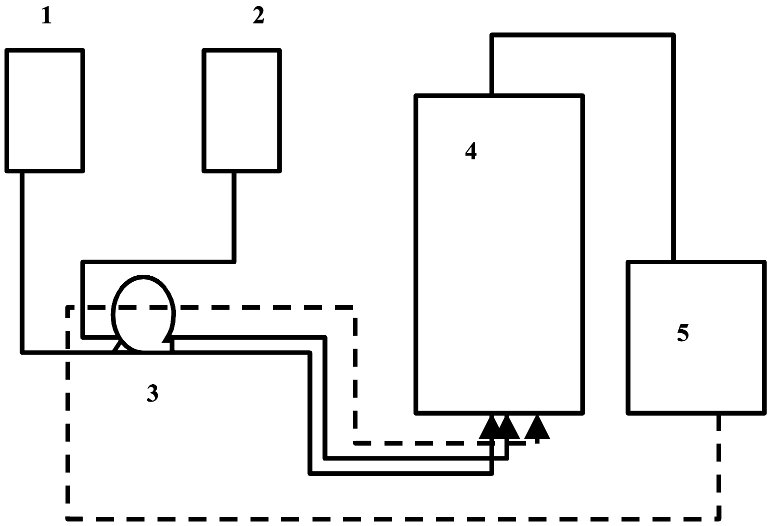

Figure 4.6 Schematic diagram of a bench-scale fluidized sand bed reactor. 1. Wastewater reservoir. 2. Na_2CO_3 reservoir. 3. Peristaltic pump. 4. Fluidized sand bed reactor. 5. Recirculation reservoir. — Initial mixing circuit. -- Recirculation circuit.

The results of these experiments indicate that no soluble rhodium was precipitated from the wastewater. In the case of the first, Figure 4.7 shows that the rhodium content halved in each replicate with minimal deviation. This is in fact, not due to removal of the rhodium by nucleated precipitation, but a dilution effect in which 1 L of approximately 100 mg/L rhodium-rich wastewater was diluted by half with sodium carbonate solution.

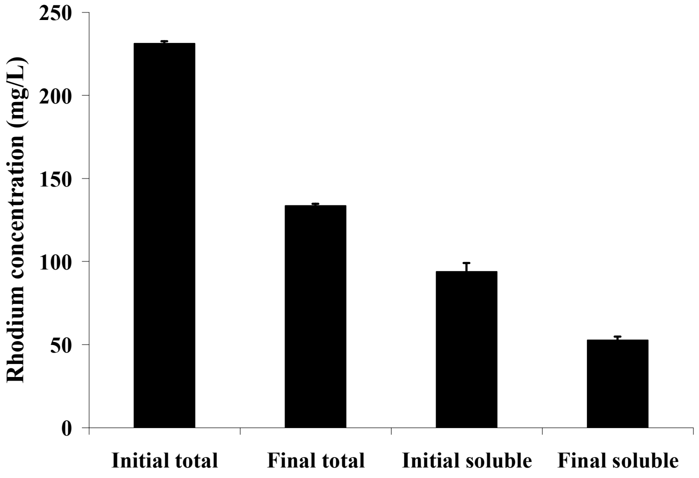

Figure 4.7 Evidence of a dilution effect. No precipitation, either nucleated or discrete occurred.

Figure 4.8 exhibits a similar trend to that seen in Figure 4.7, where the rhodium content is diluted by half. The results were consistent over 5 cycles, which indicated that the sand was never able to nucleate rhodium, either precipitated or adsorbed.

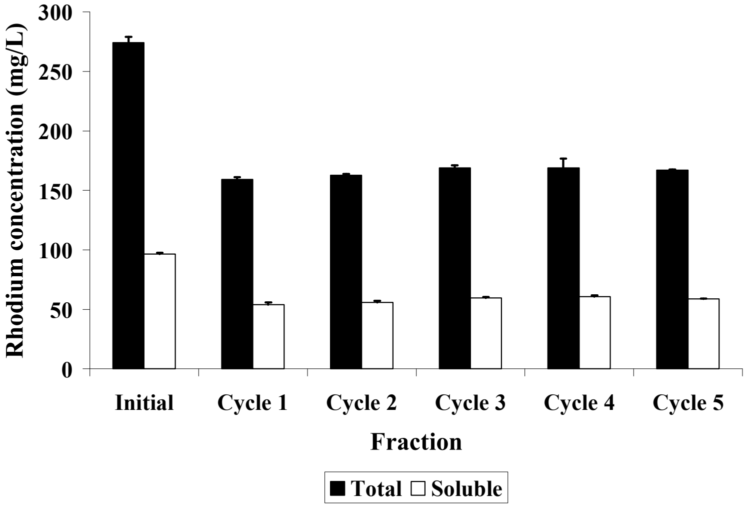

Figure 4.8 Results from the second trial indicate that the Rh(III) content, both total and soluble, was halved in each cycle via dilution with the sodium carbonate solution.

The pH of the solution is the trigger for precipitation of metals. The pH changes effected by the sodium carbonate solution on the wastewater during the sand reuse experiment are tabulated in Table 4.1. Despite the sodium carbonate solution pH of over 10, the buffering capacity of the wastewater maintained the wastewater pH below 2.

Table 4.1 The effect of the carbonate solution on the final wastewater.

	pH measurement		
	Na_2CO_3 solution	**Wastewater**	**Final Wastewater**
Cycle 1	10.99	1.30	1.65
Cycle 2	10.96	1.30	1.64
Cycle 3	10.98	1.29	1.62
Cycle 4	10.99	1.29	1.61
Cycle 5	10.94	1.25	1.63

4.5.3 DISCUSSION

An hydraulic retention time (HRT) of 7.1 minutes was used as it corresponded with the literature upon which this system was based, and as the experimental results thus far had mimicked the literature, it was expected that this HRT would yield good results. Zhou *et al*. (1999) showed that an HRT longer than 7.1 minutes produced results similar to those produced at an HRT of 7.1 minutes, with no further advantage.

It is evident from the fluidized-bed experiments that the carbonate/metal ratio alone is insufficient to initiate metal precipitation. In all cases, no precipitation occurred and all apparent metal content decreases were due to the effect of dilution. Zhou *et al*. (1999) also showed that rather than just the carbonate/metal ratio being the deciding factor for precipitation, pH played a major role in the precipitation of copper, nickel and zinc. In their experiments, the addition of the 2/1 carbonate solution raised the pH of the final wastewater to greater than 9. In this case, the 2/1 carbonate solution could not raise the pH of the wastewater by even a single pH unit, hence precluding the possibility of precipitating the rhodium ions. The lack of change in pH of the wastewater upon addition of the carbonate solution may be entirely due to the very large buffering capacity of the wastewater. Characterization of the wastewater (Appendix A) showed that very high acidity content is present (3.67 g$CaCO_3$/L), which would rapidly ‘neutralize’ any attempts to adjust the pH of the wastewater. As a consequence of this buffering, no metals would precipitate.

4.6 SUMMARY AND CONCLUSIONS

Batch studies revealed that the optimum carbonate/metal ratio could be anywhere from 1/1 to 4/1. Adsorption of rhodium ions onto sand grains does not take place in a stable or irreversible fashion. An important conclusion to be drawn from the data obtained is that the process at work here should be primarily one of precipitation.

The results also show that the fluidized bed is not capable of precipitating and removing rhodium ions from solution. Through all the bench-scale experiments, the sand was incapable of removing any of the rhodium metal contained in the wastewater.

A major indication of why the nucleation of rhodium did not take place is that the pH of the wastewater did not rise to even 2 upon addition of the sodium carbonate solution. As this rise in pH is ultimately responsible for precipitation, it is here that the experiments failed. A carbonate/metal ratio of significantly more than 2/1 seems to be required to overcome the buffering capacity of the wastewater. If an optimal carbonate/metal ratio could be found, specific to the wastewater described, capable of precipitating the rhodium at the correct rate, this may favourably alter the conclusions drawn here. If nucleated precipitation does take place, it may be worth investigating the fluidized bed reactor more closely to optimise the process and determine whether it is possible to elute the bound metal into an acid solution for reintroduction into the refinery process. If nucleated precipitation does not take place, the fluidized bed reactor is not technically viable as an alternative to the current recovery processes. All that would be achieved is precipitation of metal ions in a different environment that carries no significant advantages other than a filtration step.

CHAPTER 5

BIOSORPTION OF RHODIUM(III) FROM REFINERY WASTWATERS BY IMMOBILIZED YEAST BIOMASS

5.1 INTRODUCTION

The process of biosorption involves a solid (sorbent) and a liquid phase containing a dissolved species to be sorbed (sorbate). Depending on the affinity of the sorbent for the sorbate, the sorbate is attracted to the solid phase and bound by a number of mechanisms until equilibrium is established between the dissolved and solid-bound sorbate. The quality of a biosorbent is determined according to how much sorbate it can attract and retain in 'immobilized' form. At equilibrium, the metal uptake of the sorbent can be calculated. Metal uptake (q) can be defined as the amount of sorbate bound by the unit of solid phase, i.e. mg metal/g biomass (dry weight) (Volesky, 1990). Simple sorption models have been developed to plot and calculate q from experimental data, the simplest of which is the Langmuir Model, which expresses the relationship between q and C_f(metal concentration in solution at equilibrium):

$$q = Q_{\max}\left(\frac{bC_f}{1+bC_f}\right) \qquad \textbf{[5.1]}$$

Where: $Q_{\max}$ is the maximum metal uptake

b is a coefficient related to the affinity between sorbent and sorbate

This model is the most commonly used as it only contains two parameters ($Q_{\max}$ and b), is easily understandable and reflects the two most important characteristics of the sorption system. The Langmuir model is a model for monolayer adsorption, i.e. one must assume a surface with homogenous binding sites, equivalent sorption energies and no interaction between sorbed species (Khoo and Ting, 2001). It is important to realize that the underlying physico-chemical principles of the sorption process are not reflected in the model, the results obtained are only mathematical models capable of describing the relationship as it has been observed (Volesky, 1999). Other models include the Freundlich and Brunauer models. These are summarised in Table 5.1.

Table 5.1 Frequently used adsorption isotherm models and their advantages and disadvantages (Volesky, 2003).

Isotherm	Advantages	Disadvantages
Langmuir	Interpretable parameters	Not structured, monolayer sorption
Freundlich	Simple expression	Not structured, no levelling off
Combination (Langmuir-Freundlich)	Combination of above	Unnecessarily complicated
Radke and Prausnitz	Simple expression	Empirical, uses three parameters
Reddlich-Peterson	Approaches Freundlich at high concentrations	No special advantages
Brunauer	Multilayer adsorption; inflection point	No "total capacity" equivalent
Dubinin-Radushkevich	Temperature independent; Polanyi potential theory	Not limited behaviour in the Henry's Law regime

The rate of the uptake reaction is also vital in evaluating the sorbent of interest and it is common practice to perform simple sorption kinetics experiments to determine the exposure time required for the system to reach equilibrium. A thorough and meaningful evaluation is usually based on a combination of kinetic and equilibrium parameters. The kinetic data are of major importance as the rate of uptake has far-reaching consequences for reactor design in that a rapid uptake would require a shorter contact time, which would allow for a shallower sorbent material bed (Volesky, 1987).

The pH of the sorbate solution is considered one of the most important environmental factors affecting the biosorption process. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials. Other metal-specific influences include precipitation, speciation and the availability of the metal for biosorption (Esposito *et al.*, 2002). The response of metal ions to a biosorption process has allowed for the classification of metal ions into three classes, dependent on their behaviour at a specific pH. Class I metals (Al^{3+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, UO_2^{2+} and Zn^{2+}) are strongly bound at near-neutral pH, but are not bound or easily stripped from the biosorbent at pH < 2. This is thought to be due to electrostatic interactions between the metal ions after the ionisation of chemical functional groups such as carboxylates at these pH values. Class II metals ($PtCl_4^{2-}$, CrO_4^{2-} and SeO_4^{2-}) exhibit the opposite behaviour to class I metals. They are bound strongly at low pH and only very weakly at pH > 5. Class III metals are the most strongly bound of all metals as their binding is pH-independent (Ag^+, Hg^{2+} and $AuCl_4^-$) (Madrid and Cámara, 1997). Most metal ions present as anions in solution fall into class II and III. Precious metals (gold and PGMs) are routinely present in solution in anionic form. This implies that along with other metals present in anionic form, e.g. CrO_4^{2-}, SeO_4^{2-}, VO_4^{3-}, they are bound most strongly at low pH or exhibit pH independent binding. Niu and Volesky (2003) determined the optimal pH for adsorption of anionic gold-cyanide, selenate, chromate and vanadate to waste crab shells, all of which were found to be below 5 (gold at pH 3.4, selenium at pH 3.0, chromium at pH 2.0 and vanadium at pH 2.5). Gamez *et al.* (2003) showed the pH-independent binding pattern of $AuCl_4^-$ on to alfalfa, echoing the classification of this particular anion as class III. Both Ucun *et al.* (2002) and Bai and Abraham (2001) showed that the chromate anion binds optimally at pH < 2 on two different biosorbents, cone biomass (*Pinus sylvestris*) and *Rhizopus nigricans*, respectively. Guibal (2004), using glutaraldehyde cross-linked chitosan as an adsorbent, showed that palladium chloride adsorbs optimally at pH 2.

Despite the vast amount of literature available on metal-microbe interactions, few researchers have attempted to relate differing mechanisms and/or relative levels of uptake or toxicity to the chemical characteristics of the metal under investigation (Avery and Tobin, 1993). Pearson (1968) proposed that the differential behaviour of certain groups of metals could be attributed to differing polarizability. He conducted a survey of equilibrium values based on thermodynamic considerations, which yielded a different classification for metals according to whether they preferably complex with non-polarizable (hard) or polarizable (soft) ligands. This came to be known as the theory of hard and soft acids and bases, described in Chapter 2. Nieboer and Richardson (1980), after considering the electronegativity, charge and ionic radii of a number of metals, reached a similar conclusion and classified metal ions according to class A (hard) and class B (soft) behaviour. Hard metals are generally non-toxic and are often essential micronutrients, e.g. K^+, Na^+ and Se^{3+} (Avery and Tobin, 1993). Hard metals preferentially bind to hard ligands, usually oxygen-containing ligands (inorganic ligands such as H_2O, NO^{2-}, NO^{3-}, CO_3^{2-}, PO_4^{3-}, and polyphosphates; $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-} and ClO_4^- and organic ligands such as ethers, alcohols, phenols, ketones and carboxylates (Schwarzenbach, 1961). Soft metals exhibit greater toxicity and form stable complexes with nitrogen- or sulphur-containing ligands (Avery and Tobin, 1993). Sulphur-containing ligands include inorganic HS^- and S^{2-}, SO_3^{2-}, S_2O^{3-}, SCN^- and organic ligands such as thioethers, mercaptans and their anions, thioketones and mono-and dithiocarboxylate groups, while the nitrogen-containing ligands include primary, secondary and tertiary amines (RNH_2, R_2NH and R_3N), Schiff's bases, carboxylic amides, nitroso groups, oxime groups and azo groups (Schwarzenbach, 1961). The results of experiments performed by Avery and Tobin (1993) show that the adsorption mechanism of a range of metals to the yeast (*Saccharomyces cerevisiae*) can be related to the relative hardness or softness of the metal ion investigated.

Yeast biomass, in many forms, has been investigated for its ability to adsorb metals. Studies have shown that a number of yeast species are capable of adsorbing heavy metals such as copper, cadmium, cobalt, zinc, iron, nickel, mercury, lead, silver and chromium (Stoll and Duncan, 1997a; Zhao and Duncan, 1997; Lu and Wilkins, 1996; Wilhelmi and Duncan, 1996; Brady *et al*., 1994). Brady *et al.* (1994) also cite the ability of yeast biomass to accumulate precious metals such as gold, palladium and platinum. Lu and Wilkins (1996) compared the metal uptake properties of native yeast with a variety of immobilized forms of yeast. They found that although the native yeast adsorbed 10 – 25 % more metal, the advantages of immobilization to the process on an industrial scale, such as hardness, porosity and resistance to hydraulic pressure, still far outweighed this finding. The studies completed by Stoll and Duncan (1997a;b) compared three types of immobilization of non-viable yeast biomass. They concluded that immobilization with a combination of polyethylenimine and glutaraldehyde yielded a stable, granular biosorbent with good adsorption efficiency. This was the simplest process and also the most amenable to scale-up. Thus, these biosorbent pellets were used in further biosorption experiments in which their ability to remove copper, cadmium, chromium, nickel and zinc were tested. The results of these experiments showed that the immobilized yeast was capable of removing 75 % or more of each metal in the wastewater.

Immobilization of the biomass to be used as a biosorbent is favoured over native, free forms. This has advantages that greatly affect the efficiency of the biosorption process as a whole. The advantages inherent in the use of immobilized biomass include ease of separation of the biosorbent from a metal-laden wastewater, improved hydraulic resistance of the biosorbent for use in fixed or fluidized columns, enhancement of the physical and chemical stability of the biosorbent and enhancement of the adsorption and desorption characteristics of the biosorbent, e.g. increasing porosity by cross-linking with a polymer and extension of the metal selectivity range of the biosorbent, e.g. by addition of metal-specific ligands (Vegliò and Beolchini, 1997; Holbein, 1990). Literature describes four main techniques used in the immobilisation of biomass to produce effective biosorbents. These are entrapment in polymeric matrices, adsorption on inert supports, cross-linking and covalent bonding onto support media. *Entrapment in polymeric matrices:*

Polymers used include calcium alginate (Khoo and Ting, 2001), polyacrylamide (Wilhelmi and Duncan, 1995), polyethylenimine (Stoll and Duncan, 1997b), polysulfone and polyhydroxoethylmethacrylate. Entrapment in matrices such as these usually results in gel particles. *Adsorption onto inert supports:* This involves growing the biomass in the presence of the support, e.g. activated carbon, and thus immobilizing the biomass on the surface of the carrier (Vegliò and Beolchini, 1997). *Cross-linking:* Common cross-linking agents include formaldehyde (Zhao and Duncan, 1997), glutaric dialdehyde (glutaraldehyde) (Guibal, 2004), and divinylsulfone and formaldehyde-urea mixtures. The addition of these cross-linkers results in the formation of stable cellular aggregates and is often used to immobilize algae. *Covalent bonding onto support media*: The most common support medium used is silica gel, and the media produced is in the form of gel particles. Again, this process is used largely with algal immobilization (Vegliò and Beolchini, 1997).

For various reasons, the use of non-viable biomass in the recovery of metal ions is favoured over the use of viable biomass. These reasons include:

- No toxicity limitations,
- No growth medium or nutrient requirements,
- Desorption and reuse are possible,
- Spent biomass from local industries can be used to save costs,
- Pre-treatment in order to enhance metal binding capacity is possible,
- Simpler process control,
- Biomass can be stored for long periods (Kapoor and Viraraghavan, 1997).

In addition, many studies comparing the adsorption capacities of viable and non-viable biomass have shown that the non-viable biomass can adsorb far greater amounts of metal, e.g. Horikoshi *et al.* (1979) showed that killed algal cells biosorbed more than three times more uranium than the living cells. Table 5.2 provides a small number of examples of biomass that have been used successfully in a non-viable form

Table 5.2 Examples of biomass types used as a biosorbent in a non-viable form.

Biosorbent	**Target metal**	**Reference**
Mucor rouxii	Pb, Zn, Cd, Ni	Yan and Viraraghavan, 2003
Rhizopus nigricans	Cr	Bai and Abraham, 2002
Activated sludge	Cu, Zn	Utgikar *et al*., 2000
Phormidium laminosum	Cu, Fe, Ni, Zn	Blanco *et al*., 1999

5.2 HYPOTHESIS

An immobilized, non-viable yeast biosorbent system is capable of efficiently adsorbing rhodium(III) metal from process wastewaters, and is a feasible alternative to current physico-chemical methods.

5.3 AIMS AND OBJECTIVES

The overall aim was to investigate the application of immobilised yeast for the recovery of rhodium(III) from process wastewaters. In order to achieve this, the following four objectives were set:

- Optimize the production of immobilized yeast biosorbent.
- Determine the efficiency of the yeast biosorbent for the recovery of rhodium ions from pure aqueous solutions.
- Determine the degree of difference expected when treating a wastewater solution rather than a pure solution.
- Investigate the efficiency of the biosorbent in a fixed-bed column configuration.

5.4 IMMOBILIZATION OF YEAST BIOMASS TO FORM AN EFFICIENT BIOSORBENT

As stated previously, immobilized biomass is generally favoured over free forms. In the current study, yeast biomass has been immobilized for many of the purposes stated. The specific advantages to be gained include the easy recovery of the biosorbent from solution; the use of the biosorbent in fixed-bed columns without showing signs of deficiency, resistance to dilute chemical degradation and high adsorption capacity for metal ions.

5.4.1 MATERIALS AND METHODS

Yeast biomass (*Saccharomyces cerevisiae*) was obtained from a bakery supplied by Anchor Yeast Inc. and was used in the preparation of immobilized yeast pellets. All reagents were of laboratory grade. All glassware was acid washed in 5 % HNO_3 and rinsed in distilled water before use. Rhodium(III) metal solutions were made up by diluting a 1000 mg/L rhodium atomic adsorption standard solution (Fluka, Switzerland) with distilled water until the desired concentration was reached.

Immobilization of yeast biomass

Compressed bakers yeast was immobilized using a process defined by Stoll (1996) using polyethylenimine (PEI) (50 % aqueous polyethylenimine, Sigma-Aldrich, Germany) and glutaraldehyde (GA) (50 % aqueous gluteraldehyde, Sigma-Aldrich, Germany), with subsequent treatment with hot alkali (3 % potassium hydroxide) solution.

Immobilization

An initial ratio of PEI :GA :yeast (ml :ml :g) of 1.2:1:40 was found to be optimal in the process designed by Stoll (1996). As such, 40 g (wet weight) of yeast was hand-mixed with 4 ml distilled water to form a smooth paste. This paste was then treated with the embedding and cross-linking agents. A 25 % (v/v) solution of GA was added to the yeast-paste and blended until smooth. 33 %

(v/v) PEI was added and the mixture was blended until moist dough was obtained. This dough was then crumbled to form granules and the granules were dried overnight at 80 ºC.

Hot alkali treatment

The immobilized yeast pellets were suspended in 3 % (w/v) KOH solution and heated to 70 ºC in a water bath. The granules were then settled and separated from the caustic solution. The caustic solution was retained and the biomass was washed twice with distilled water (the wash water being added to the caustic solution each time). The alkali-soluble components of the biomass were reconstituted by acidification of the caustic solution with 32 % HCl. The HCl was added with stirring until a pH of 6.0 was reached. Subsequent centrifugation (4000 g for 10 min) (Centrifuge 5403, Eppendorf, Germany) pelleted out the reconstituted biomass. The washed and reconstituted biomass was then added to the alkali-insoluble fraction and both were dried overnight at 80 ºC.

Immobilization necessity

The immobilization process, although the simplest investigated by Stoll (1996), is extremely labour-intensive. The necessity for the complete immobilization process was tested by comparing the yeast produced at each stage of the immobilization. The immobilization reagents were also tested in the absence of biomass to ascertain the degree of adsorption that could be attributed to the reagents alone. The types of pellet formed as well as the stability of the pellet were compared before simple adsorption tests were performed to determine which stage adsorbed the most rhodium and whether or not the reagents used in the adsorbent production contributed to the efficiency. Removal efficiency was determined by a simple adsorption experiment in which 0.25 g (triplicate) of biomass from each treatment was exposed to 50 ml of a 30 mg/L rhodium solution for 1 hour (200 rpm agitation (Labcon shaker, South Africa)). After incubation, a 5 ml sample was filtered through 0.45 µm pore size cellulose-acetate filter (Whatman, England) paper the pH was adjusted to below 2, and the rhodium concentration left in solution was determined using an atomic absorption spectrophotometer (AAS).

Process variation

Variation between batches of immobilized biomass was investigated to determine the reproducibility of the percentage yield and removal efficiency of the adsorbent. Ten 40 g batches were produced within two days of each other in order to limit external environmental factors such as ambient temperature and humidity. Each batch was treated as described earlier and stored separately. Two factors were used to determine the degree of variation between each batch; these were percentage yield and removal efficiency. The percentage yield was calculated as the final (dry) weight of the adsorbent expressed as a percentage of the initial (wet) weight of the yeast. Removal efficiency was determined by a simple adsorption experiment in which 0.25 g (triplicate) of biomass from each batch was exposed to 12.5 ml of a 30 mg/L rhodium solution for 1 hour (200 rpm agitation). After incubation, a 5 ml sample was filtered through 0.45 µm cellulose-acetate filter paper the pH was adjusted to below 2, and the rhodium concentration left in solution was determined using atomic absorption spectrophotometry.

Sensitivity to scale-up

The ability of the adsorbent to retain a high efficiency despite the scale-up of the production process is extremely important. This factor was investigated by producing batches of 40 g, 80 g and 120 g initial yeast biomass. Ten replicate batches at each size were produced, all within a short time interval to limit external influences. Again, two factors were analyzed, percentage yield and removal efficiency. A small portion (0.25 g) from each batch was exposed to 12.5 ml of a 30 mg/L rhodium solution for 1 hour (triplicate), shaking at 200 rpm. After incubation, a 5 ml sample was filtered through 0.45 µm cellulose-acetate filter paper, the pH was adjusted to below 2, and the rhodium concentration left in solution was determined using an AAS. The results from each size class were then compared.

Granule size effects

The results obtained in the preceding experiments seemed to suggest that the heterogeneity of the granule sizes used in the experiments was the reason for the differences between batches and between scaled up batch sizes. This theory was investigated by grading the granules through a 2 mm sieve. The removal efficiency of the < 2 mm diameter granules (that fell through the sieve) was compared to the efficiency of the > 2 mm diameter granules (that did not pass through the sieve). Again, triplicate 0.25 g samples from each sieve category were exposed to 12.5 ml of a 30 mg/L rhodium solution for 1 hour, shaking at 200 rpm. After incubation, the samples were treated as stated above. The removal efficiencies of the granule size categories were compared to determine the effect of granule size, and hence available surface area, on the adsorption of rhodium from aqueous solution.

5.4.2 RESULTS

Immobilization necessity

Figure 5.1 showed that an increase of almost 20 % was achieved by fully processing the yeast (Immob and Alkali Yeast) compared to just drying it. A major trend seen in the graph was the removal efficiency of the immobilization media, 85 and 90 % respectively. However, the pH of those experiments showed conclusively, that this removal was due to precipitation and not adsorption. The neutralized biomass showed almost identical removal efficiency to the un-neutralised biomass. *Azolla filiculoides,* an aquatic weed, was also tested out of interest as this biomass showed high affinity for both platinum and gold in previous studies (Antunes *et al*., 2001; Antunes, 2002). The alkali treated yeast showed little removal despite increasing the solution pH to greater than 6. It is not understood exactly why this result does not conform to the increased pH = precipitation trend.

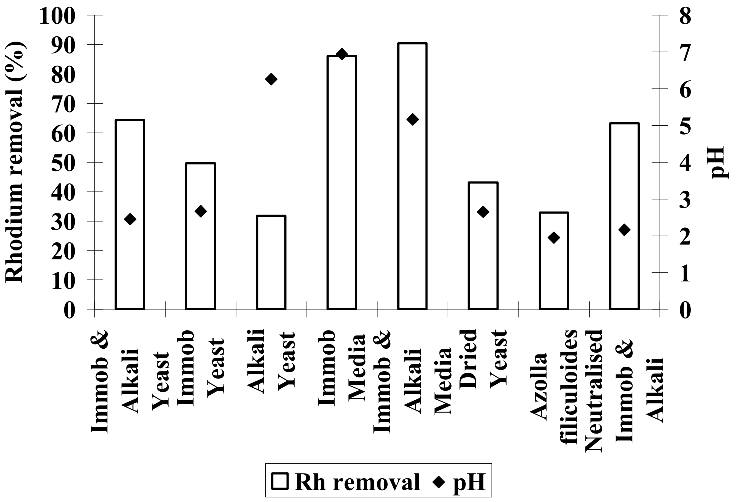

Figure 5.1 Comparison of the various stages of the yeast biosorbent production process.

Process variation

When formulating the biosorbent, the process is simple and easily repeatable. The only variation between batches would come from the human factor, this being mixing efficiency and formation of different granule sizes. Two factors were analysed in this experiment. The first, percentage yield, showed little variation, the average being 21.44 % (ten replicates, SD = 1.54 %). The full data set is reported as part of the scale-up experiment, Table 5.4. The second factor of interest was removal efficiency when exposed to a rhodium-containing solution. Figure 5.2 shows removal efficiencies of between 33 and 42 %, with an average of 37 % of the rhodium in solution adsorbed to the biomass. The standard deviation is quite high, at 2.3 %.

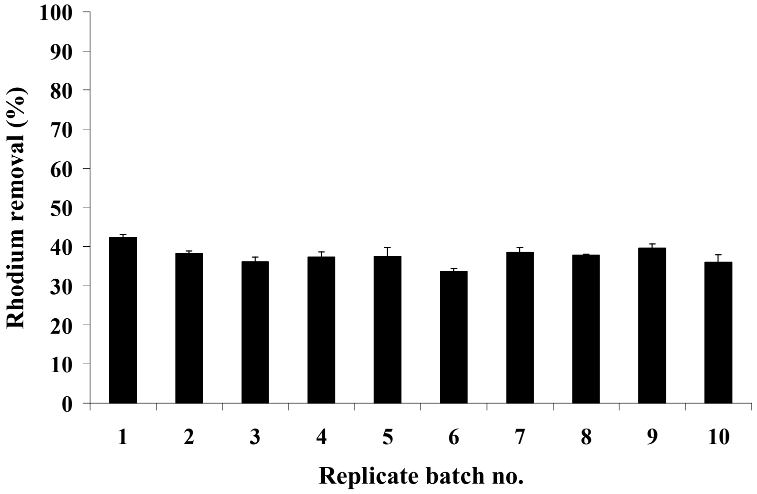

Figure 5.2 Removal efficiency compared over ten batches of 40 g initial yeast wet weight. Each batch result is an average of triplicates and all errors are below 2.5 %.

This is supported by the results of a statistical analysis performed on the data (Table 5.3). This one-way ANOVA analysis shows that by calculating an F value much higher than the critical F value, the null hypothesis, i.e. no difference between the means, can be rejected and it can be concluded that there is a significant difference between the mean removal efficiencies of each batch.

Table 5.3 Output table showing results of a one-way ANOVA, indicating that there is a significant difference between the means of each batch (ά = 0.05, *n* = 10).

Source of variation	***SS***[1]	***df***[2]	***MS***[3]	***Calculated F-value***	***P-value***	***Reference F-value***
Between groups	143.06	9	15.90	9.81	1.33×10^{-5}	2.39
Within groups	32.42	20	1.62			
Total	175.49	29				

[1] sums of squares, [2] degrees of freedom (*n*-1), [3] mean square (*SS*/*df*).

Sensitivity to scale-up

The effect of scaling up a production process, the results of which seem to be highly dependent on the efficiency of the mechanical input, must be investigated to determine whether the efficiency of the product is affected by the use of a larger starting mass. In this case, it was not practically possible to increase the batch sizes beyond 120 g of yeast due to laboratory equipment constraints. In Table 5.4, the full percentage yield data is presented for all batches and batch sizes produced. The average yield at each size does not decrease or increase significantly as the size increases. A yield of approximately 20 % was achieved at each starting mass.

Table 5.4 Percentage yield data for all batches and batch sizes produced.

Batch number	Yield (as % of initial yeast weight)		
	40 g	**80 g**	**120 g**
1	21.00	20.97	20.92
2	21.50	17.26	21.65
3	21.46	19.09	19.96
4	24.90	17.61	21.06
5	20.74	17.08	20.90
6	22.74	20.25	22.87
7	21.88	16.53	22.38
8	20.55	18.23	24.04
9	20.49	21.50	24.40
10	19.16	20.69	23.81
Mean	**21.44**	**18.92**	**22.20**
SD	1.54	1.82	1.54

In Figures 5.2, 5.3 and 5.4, the removal efficiencies of the batches produced using 40 g, 80 g and 120 g initial yeast wet weights are shown. There is a significant increase in the efficiency of the batches produced using 80 g over those produced using 40 g initial wet weights (37 % average to 73 % average), and a smaller increase at 120 g (73 % average to 78 % average).

Statistical analysis of the data showed that significant differences existed between the means of each batch using 120 g wet weight. However, in the batches made using 80 g of yeast, no significant difference was found between the means (results summarized in Table 5.5). This may suggest that at 80 g, the most uniform-sized granules are produced. However, it may also be an artefact resulting from more careful pre-drying granulation or more careful selection of smaller granules for the experiment

Table 5.5 Summarized results of one-way ANOVA performed on data resulting from various batch sizes (ά = 0.05, *n* = 10).

	Between groups variation			
Batch size	**Calculated F-value**	**P-value**	**Reference F-value**	**Significant difference**
40 g	9.81	1.33×10^{-5}	2.39	Yes
80 g	2.07	0.08	2.39	No
120 g	16.63	1.91×10^{-7}	2.39	Yes

In Figure 5.3, the removal efficiency has almost doubled compared to that achieved using the 40 g batches (Figure 5.2). The increase from an average removal of 37 % to one of 73 % may be attributable to a larger proportion of small granules present in the experimental flasks.

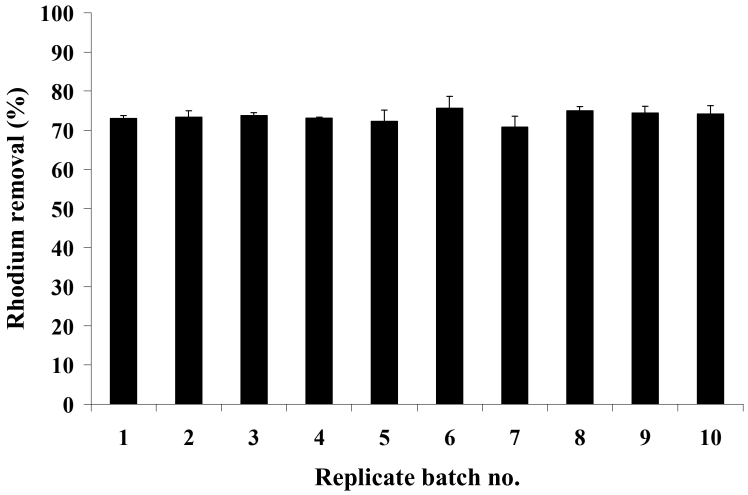

Figure 5.3 Removal efficiency compared over ten batches of 80 g initial yeast wet weight. Each batch result is an average of triplicates and all errors are below 3.0 %.

A much smaller increase was achieved using the larger initial mass, only 5 % more rhodium was adsorbed than for the 80 g batches.

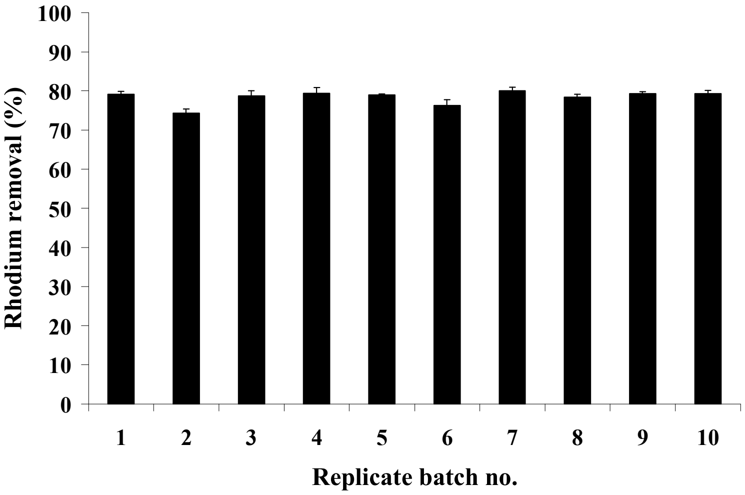

Figure 5.4 Removal efficiency compared over ten batches of 120 g initial yeast wet weight. Each batch result is an average of triplicates and all errors are below 1.5 %.

Granule size effects

The results obtained in the preceding experiments seemed to suggest that the heterogeneity of the granule sizes used in the experiments was the reason for the differences between batches and between scaled up batch sizes. This hypothesis was investigated by grading the granules through a 2 mm sieve. Figure 5.5 shows that an increase in removal of approximately 20 % can be achieved by using granules with diameters smaller than 2 mm.

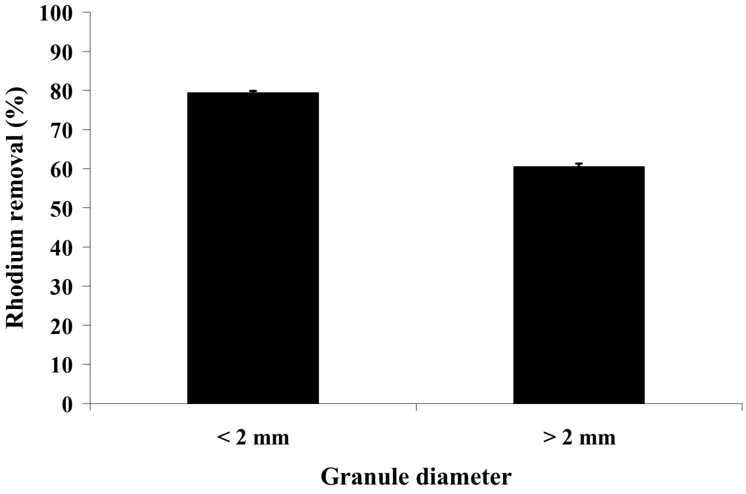

Figure 5.5 Comparison between adsorption capacities of granules smaller or larger than 2 mm diameter.

5.4.3 DISCUSSION

Immobilization of biomass by cross-linking in a polymeric matrix is known to yield beads or granules of optimum size, mechanical strength, rigidity and porosity (Lu and Wilkins, 1996). The use of polyethylenimime (PEI) and glutaraldehyde (GA) produced granules of variable size, but the granules did exhibit mechanical strength and proved resistant to dilute acids. Other methods used to immobilize yeast include polyacrylamide gels (Wilhelmi and Duncan, 1996; Brady and Duncan, 1994), polyvinylalcohol sodium orthophosphate beads (Stoll and Duncan, 1997a), sodium alginate beads (Stoll and Duncan, 1997a; Lu and Wilkins, 1996) and formaldehyde cross-linking (Zhao and Duncan, 1997).

Metal uptake analyses of the stages of immobilization and the immobilizing agents themselves were completed, firstly to determine if the full immobilization and alkali treatment is necessary, and secondly to determine what (if any) biosorption effects can be attributed to the immobilizing agents, i.e. PEI and GA. Figure 5.1 showed a progression of increasing metal uptake capacity as the biomass moved through the process. Dried yeast removed approximately 45 % of the soluble rhodium available, after immobilization, this increased to 50 % and after alkali treatment, the removal was approximately 70 % of the rhodium in solution. It seemed that the immobilization process did not adversely affect any surface binding sites for adsorption but, conversely, seemed to improve the availability of these sites. In the case of the immobilizing agents, the apparent high metal removal could be attributed to the increase in solution pH rather than an adsorption phenomenon.

The factors investigated when determining the inherent variation in the yeast biosorbent production process were percentage yield and metal uptake efficiency. The average percentage yield per batch of yeast was 21.44 % (dry weight) when using an initial mass of 40 g (wet weight) (Table 5.4). This result is higher than the percentage yield reported by Stoll (1996), who achieved a yield of between 15 and 17 % using the same process. This may be due to the different form of biomass used in the study by Stoll (1996), in which the biomass had not been compressed into cakes for sale to bakeries. The area of largest weight loss, according to Stoll (1996), is the alkali treatment. Caustic or alkali treatment of yeast reduces the production yield for a number of reasons. It removes lipids and proteins on the cell surface that would otherwise mask reactive sites (Brady *et al.*, 1994). However, a considerable amount of the protein removed is manno-protein, which can be retrieved through reconstitution of the alkali-soluble fraction by adjusting the pH of the wash solutions (Lu and Wilkins, 1996). A further advantage is the destruction of autolytic enzymes that would otherwise putrefy the biosorbent during storage. Brady *et al.* (1994) suggest that the remaining biomass consists of mainly glucan and chitosan, with most of the chitin converted to chitosan by the hot alkali. Although caustic treatment is thought to increase the metal uptake capacity of the biomass, Galun *et al.* (1987) showed that pre-treatment of *Penicillium* biomass with alkali greatly reduced the metal uptake.

The statistical difference between the mean rhodium uptake capacities of the 40 g initial yeast batches was expected (Table 5.3), as it was noted early on in the study that the granules produced were not of a uniform size, but depended on the efficiency of mixing and pre-drying granulation. This factor was found to exert a major effect on the efficiency of the biosorption process.

When scaling up the production process, the same two factors were investigated. The percentage yield achieved with the 80 and 120 g batches were 18.92 and 22.20 %, respectively (Table 5.4). When averaging the percentage yields across the different initial yeast masses, the result is an approximate 20 % yield with a standard deviation of only 1.6 %. Thus, in terms of yield, scaling up the production process does not seem to affect the efficiency of the product. However, the metal uptake capacity increased hugely from the 40 g (37 % removal on average (Figure 5.1)) to the 80 g (73 % removal on average (Figure 5.2)) batches and only slightly again from the 80 g to the 120 g (78 % removal on average (Figure 5.3)) batches. These increases were tentatively concluded to be caused by variation in the size of the granules produced, as it was noted that the larger batch sizes seemed to produce smaller granules on average than the 40 g batches. Statistical analysis of the batches showed that variation existed within both the 40 and 120 g mass classes (Table 5.5). This was again attributed to micro-variations in the size of the granules produced, i.e. one batch yielding smaller granules than another. The fact that there was no statistical difference between the metal uptake means for the batches produced from 80 g initial yeast biomass may suggest that at this initial mass the most uniform-sized granules were produced.

From the preceding experiments, it was clear that variation in metal uptake capacity was a disadvantage of the production process. This variation was thought to be introduced via the size of the granules formed in each batch. Exploration of this idea lead to the discovery that if the granules were pooled and separated according to size, granules with a diameter less than 2 mm showed a 20 % higher adsorption capacity than those with a larger diameter (Figure 5.4). Volesky (2001) suggests that, like ion exchange resins manufactured for the same purpose, good biosorbents should generally feature particle sizes of between 0.7 and 1.5 mm, particularly if the process is based on a fixed-bed reactor configuration, where the sorption bed needs to be porous enough to allow liquid through with minimal resistance while allowing maximum mass transfer into the particles.

5.5 BATCH STUDIES USING PURE RHODIUM(III) SOLUTION

The affinity of the formulated yeast biosorbent for rhodium metal ions was initially determined using a pure rhodium solution. This investigation provided an indication of a ‘best case scenario’ when using the yeast biosorbent to accumulate mixed rhodium ion species from an aqueous solution, as the rhodium ions are in their most extractable form, $RhCl_6^{3-}$.

5.5.1 MATERIALS AND METHODS

Yeast biosorbent material was produced as described in section 5.4.1 (40 g initial mass, full immobilization, < 2 mm granule diameter). All reagents were of laboratory grade. All glassware was acid washed in 5 % HNO_3 and rinsed in distilled water before use. Rhodium metal solutions were made up by diluting a 1000 mg/L rhodium atomic adsorption standard solution (Fluka, Switzerland) with distilled water until the desired concentration was reached.

Adsorption kinetics

Aliquots of 50 ml of pure rhodium solution (65 mg/L) were placed into three 100 ml conical flasks. The experiment was initiated by the addition of 2 g of biomass to each flask. A blank was run concurrent to the experiment without biomass, to account for any adsorption of the rhodium to the glassware or spontaneous precipitation of the metal ions. All flasks were agitated at 200 rpm on a bench top shaker (Labcon, South Africa). Samples (2 ml) were taken at regular intervals (0, 5, 10, 30, 60, 90, 120, 180 minutes). These were then filtered through 0.45 µm pore size cellulose acetate filters (Whatman, England) and the removal of rhodium was determined using atomic absorption spectrophotometry (GBC 909 AA, Avanta, Australia).

Adsorption isotherm

Adsorption isotherms were constructed according to the subsequent addition method (SAM) described by Pagnanelli *et al*. (2000) and detailed in section 4.4.1.

Comparison between adsorption of rhodium from wastewater and from pure solution

Two sets of triplicate flasks were prepared, each containing 50 ml of wastewater (Rh concentration of approximately 50 mg/L) or 50 ml of rhodium solution (50 mg/L). The experiment was initiated by the addition of 1 g of yeast biomass. All flasks were agitated at 200 rpm on a bench top shaker. After 1 hour, samples (3 ml) were taken and treated as stated previously and assayed for rhodium content. The results allowed for a comparison between the adsorption of rhodium from a pure solution with that of wastewater.

5.5.2 RESULTS

Adsorption kinetics

In order to construct an isotherm to determine the maximum uptake of metal per gram of biomass, it was necessary to first determine the time taken for the metal concentration to reach equilibrium between the biomass and the solution. This time would then become the incubation period between additions of metal solution to the isotherm experiment. Figure 5.6 shows an extremely fast adsorption of rhodium onto the biomass. Within 15 minutes, the metal concentration had reached equilibrium at a percentage removal of approximately 50 %. This remained stable for the duration of the experiment, indicating a strong bond between metal and biomass.

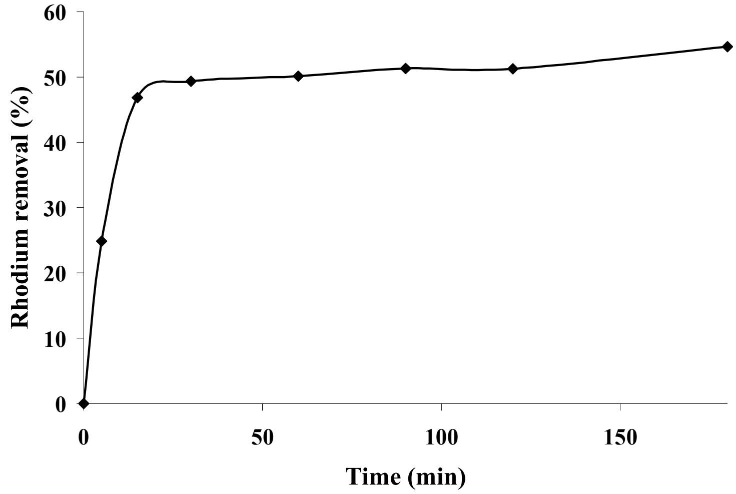

Figure 5.6 Adsorption kinetics curve (average of triplicate experiment, error bars not visible, SD < 1 %) showing the time taken for the unbound metal concentration to reach equilibrium.

Adsorption isotherms

In Figure 5.7, the data resulting from the isotherm experiment are shown. The result showed that the uptake at pH 2 and 3 was much more stable than at pH 1. It was also clear from the data that the metal uptake capacity was slightly higher at pH 3. This could be deduced from the graph by comparing the values of *q* at which the curves begin to level off. The possibility of spontaneous precipitation was eliminated by the negative control experiments (i.e. no biomass) performed at each pH, which showed no spontaneous precipitation (Appendix B).

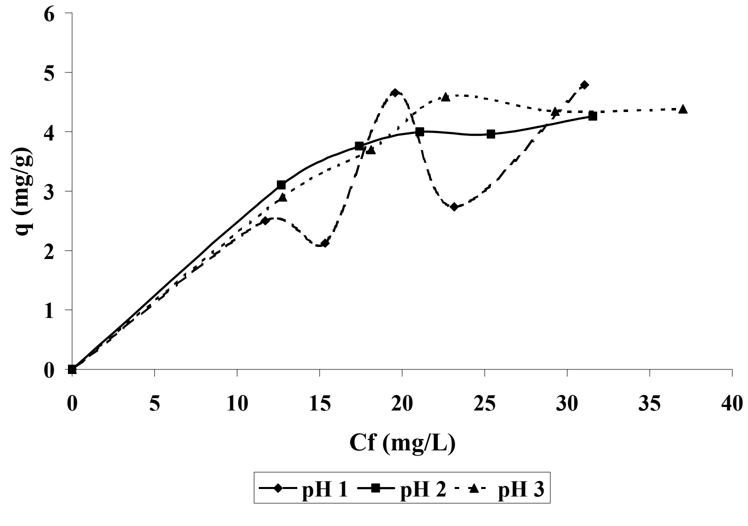

Figure 5.7 Data obtained from the adsorption isotherm experiment, showing the higher metal uptake (*q*) at pH 3.

By plotting the reciprocal of the C_f and q values for the isotherm, the data were linearized and fitted to the Langmuir isotherm model to produce two values; the Q_{max} (maximum metal uptake per gram of biosorbent), and b (the affinity of the metal for the biosorbent) at each pH. Figure 5.8 again illustrates the stable nature of the isotherms at pH 2 ($R^2 = 0.93$) and 3 ($R^2 = 0.85$), and the apparent non-fitting data at pH 1 ($R^2 = 0.44$). The parameters calculated as a function of the pH of the metal solution are shown in Table 5.6.

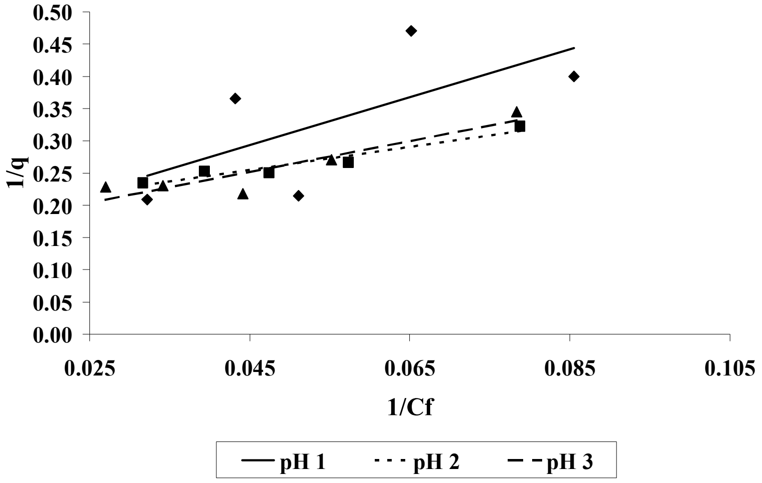

Figure 5.8 Linearized data from the adsorption isotherm, showing the fit of the data at pH 2 (■) and 3 (▲) and the non-fit at pH 1 (♦).

At pH 1, both the calculated Q_{max} and b values were high. A high Q_{max} value is desirable in a biosorbent, but a high b value is not. The very low R^2 value also seemed to indicate that the data did not fit a straight line and, so could not be compared to the data obtained at pH 2 and 3. As indicated by the R^2 values, these data closely matched the trend line and in comparing them it was seen that the most favourable values were achieved at pH 2. At this pH there was a higher Q_{max} (6.99 mg/g) than at pH 3 (5.74 mg/g), but the metal/biosorbent affinity was lower (16.75 at pH 2 vs. 10.29 at pH 3).

Table 5.6 Langmuir isotherm parameters calculated from constructed adsorption isotherm.

pH	**Equation of linearization**	**R^2**	***Q*max (mg metal/g biosorbent)**	***b* (affinity of metal for biosorbent)**
1	y = 3.72x + 0.13	0.44	7.97	29.67
2	y = 1.79x + 0.17	0.93	6.99	16.75
3	y = 2.40x + 0.14	0.85	5.74	10.29

Comparison between adsorption of rhodium from wastewater and from pure solution

Figure 5.9 indicates a decrease in uptake by more than 50 % when the biosorbent is exposed to wastewater compared to the average uptake from pure rhodium solution (70 %). This may be due to a number of possibilities including 1) a different compound binding preferentially to the sites available to rhodium, and 2) a compound present in the wastewater acting as a strong metal ligand and preventing the binding of the metal ions to the biosorbent.

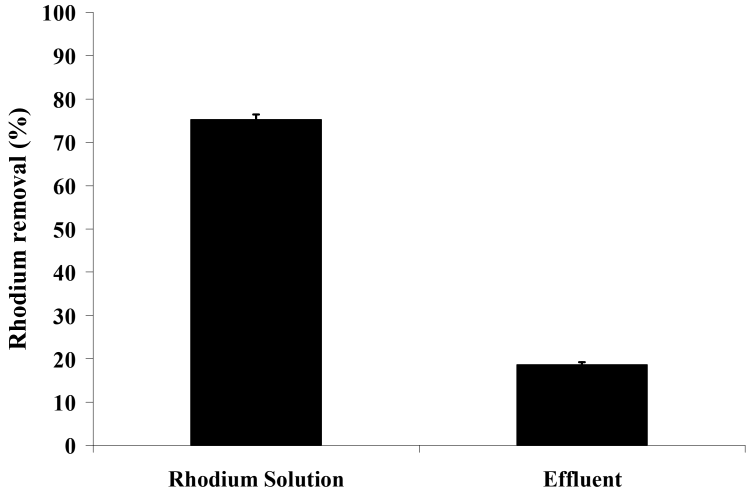

Figure 5.9 A comparison between rhodium adsorption from a pure solution and from the wastewater solution. This shows a great difference in response to the biosorbent.

5.5.3 DISCUSSION

Metal accumulation by biosorbents has often been shown to consist of two phases, a rapid initial phase lasting 5 - 30 minutes, and a slower phase that may only equilibrate after 24 - 48 hours (Sheng *et al.*, 2004; Ucun *et al.*, 2002). Brady and Duncan (1994) showed that copper accumulation by immobilized viable yeast cells followed a similar pattern. They found that the second phase did not occur if the copper: yeast ratio was below a threshold level, which they suggested demonstrated two discrete processes; one of simple biosorption to the cell wall, and a second possibly involving metal internalization by the cells. Sheng *et al.* (2004) put forward a number of cases where similar patterns are found in non-viable biomass biosorption experiments, but that the first process was mainly ion exchange and the second process was one of microprecipitation and/or adsorption. Figure 5.6 indicates a rapid uptake of rhodium from solution. After 15 minutes, an equilibrium metal concentration of approximately 30 mg/L remained in solution. Such rapid adsorption is common and is indicative of passive adsorption to cell surfaces. This 15-minute adsorption time is mirrored in most, if not all biosorptive processes. For example, Zhao *et al*. (1997) recorded that 80 % of the nickel bound to the aquatic weed, *Azolla filiculoides,* was bound within the first 10 minutes of the kinetics study. Similar results were found, again with *Azolla filiculoides* by Antunes *et al*. (2001), where extremely rapid removal of gold from solution occurred within 20 minutes. In applying a process to ‘real world’ conditions, this rapid adsorption phase is considered advantageous since the shorter contact time allows for smaller rapid flow-through contactor equipment, resulting in positive benefits for both capacity and operation costs (Sheng *et al*., 2004). This rapid equilibration time is an important indicator used in the construction of adsorption isotherms that determine process parameters such as maximum metal uptake (mg) per gram of biosorbent and give an indication of the affinity of the biosorbent for the metal of interest. As stated in the methods section for this experiment, adsorption isotherms built according to the subsequent addition method (SAM) require an equilibration time. This time is found by performing the adsorption kinetics experiment discussed previously.

An adsorption isotherm yields data regarding not only the maximum specific uptake of metal per gram of biomass, but also an indication of the binding affinity of the biomass for the metal ions in question. A good biosorbent would typically exhibit a high $Q_{\max}$ value and a low b value. If this premise is to be held true, a pH of 2 yields an optimal result in a trade-off between metal uptake and affinity. This pH falls within the same range as other anionic metal ions such as chromate (pH 2.0), vanadate (pH 2.5), gold (pH 3) (Niu and Volesky, 2003) and platinum (pH 2) (Antunes, 2002).

Up to this stage, all experiments were performed using a pure rhodium solution. As this is often not a true reflection of how the metal will respond in a wastewater, it was necessary to determine whether the pure metal solution did indeed mimic the behaviour of the rhodium in the wastewater. Figure 5.9 shows quite clearly that it did not. Only 20 % of the soluble rhodium in the wastewater was adsorbed compared to almost 75 % in the pure solution. The wastewater environment is often extremely different to the environment in which the biosorbent is first tested.

5.6 BATCH STUDIES USING WASTEWATER

As stated previously, the wastewater environment is never as simple to bioremediate as the artificial laboratory environment. In this case it has been proved true by the experiment comparing removal efficiency of the biomass in pure rhodium solution with its efficiency in wastewater. Further investigation is required to determine the cause/s of the lower efficiency in order to optimize the environment for more efficient recovery of rhodium.

5.6.1 MATERIALS AND METHODS

Yeast biosorbent material was produced as described in section 5.4.1 (40 g initial mass, full immobilization, < 2 mm granule diameter). All reagents were of laboratory grade. All glassware was acid washed in 5 % HNO_3 and rinsed in distilled water before use. Rhodium-laden wastewater was provided by a precious metal refinery and stored in airtight containers at room temperature until use.

Adsorption kinetics

Aliquots of 50 ml of wastewater (65 mg/L) were placed into three 100 ml conical flasks. The experiment was initiated by the addition of 2 g of biomass to each flask. A blank was run concurrent to the experiment without biomass, to account for any adsorption of the rhodium to the glassware. All flasks were agitated at 200 rpm on a bench top shaker (Labcon, South Africa). Samples (2 ml) were taken at regular intervals (0, 5, 10, 30, 60, 90, 120, 180 minutes). These were then filtered through 0.45 µm pore size cellulose acetate filters (Whatman, England) and the removal of rhodium was determined using atomic absorption spectrophotometry (BC 909 AA, Avanta, Australia).

Adsorption isotherm

As described in section 5.5.1, adsorption isotherms were constructed according to the SAM method (Pagnanelli *et al.*, 2000) described briefly in section 4.4.1. Five additions were made, using the equilibration time determined in section 5.5. Aliquots (2 ml) of 65 mg/L rhodium wastewater were added in place of the pure rhodium solution.

Effect of suspended solids in wastewater on adsorption of rhodium

A 200 ml sample of wastewater was centrifuged at 4000 rpm for 10 minutes and the supernatant was decanted and used in an experiment to determine the effect of suspended solids on adsorption. 50 ml aliquots of either centrifuged or non-centrifuged wastewater were placed in 100 ml conical flasks. Flasks were prepared in triplicate and the experiment was initiated by the addition of 1 g of yeast biomass. All flasks were agitated at 200 rpm on a bench top shaker. After 1 hour, samples were taken from each flask (treated as stated previously) and assayed for rhodium and the resulting removal efficiencies compared.

Effect of precious metal anion interference on rhodium adsorption from wastewater

A wastewater sample was analyzed for the presence of other precious metals that may interfere with rhodium adsorption. The metals found in the highest concentration were gold (Au) and palladium (Pd). The effect of the presence of these metals was determined by comparing the adsorption of each metal under three conditions, a) as a single-metal solution at the concentration at which the metal is present in the wastewater, b) in a pure-metal mixture at the concentrations at which the metals are present in the wastewater, and c) in the wastewater itself. 50 ml aliquots of each single-metal, mixture, or wastewater were placed in 100 ml conical flasks and the experiment was initiated by the addition of 2 g of yeast biomass. All flasks were agitated at 200 rpm on a bench top shaker. After 20 minutes, samples were taken and treated as stated previously. Metal concentrations were analyzed using atomic absorption spectrophotometry.

5.6.2 RESULTS

Adsorption kinetics

Similar to the rate curve produced with the pure rhodium solution, a rapid uptake was noted in the wastewater experiment (Figure 5.10). Within the first 30 minutes equilibrium had been reached. This was, again, at a much lower bound metal concentration than was achieved with the pure rhodium solution. Equilibrium was attained with less than 10 % of the available rhodium bound to the biosorbent.

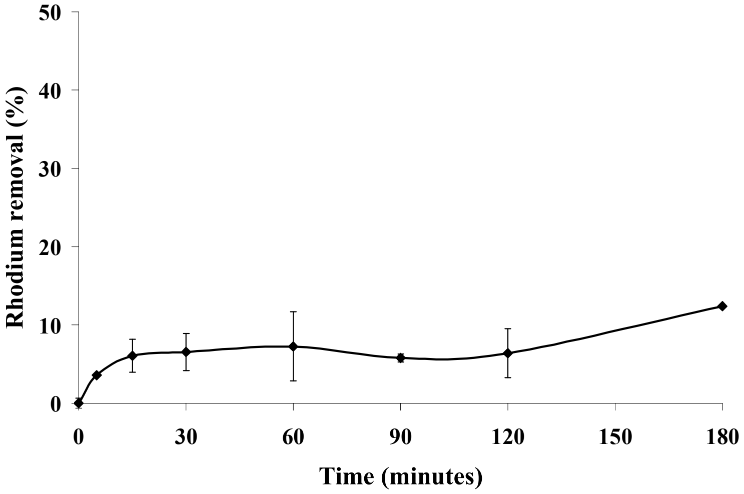

Figure 5.10 Adsorption kinetics curve (mean of triplicate experiment, SD visible when greater than data point dimensions) showing the time taken for the bound metal fraction in the wastewater to reach equilibrium with the unbound fraction.

Adsorption isotherm

The adsorption isotherm constructed using wastewater (Figure 5.11) showed a seemingly identical pattern at each pH. Negative control experiments run concurrently proved that no precipitation effects were erroneously represented as adsorption (Appendix 2). The maximum uptake capacity (*q*) did not appear to be affected by pH at levels of 3 and below.

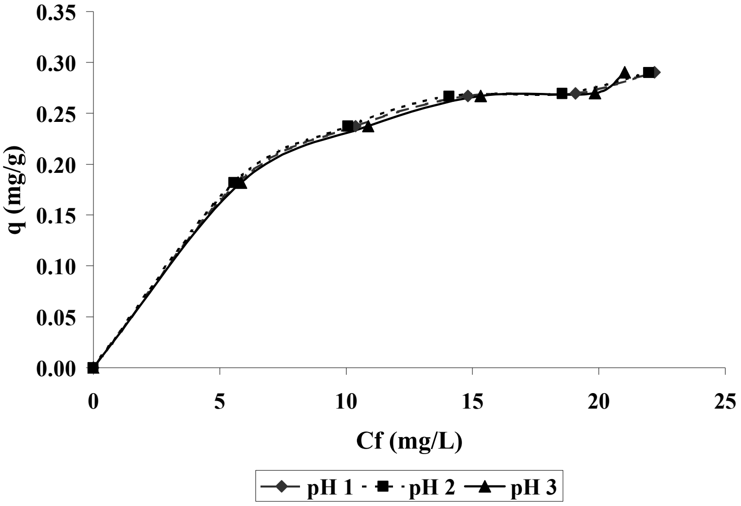

Figure 5.11 Data from the wastewater adsorption isotherm, showing an identical pattern at each pH.

The linearized data (Figure 5.12) only serve to reiterate this theory, in that the linearized data, and hence the calculated parameters were the same at all pH levels investigated.

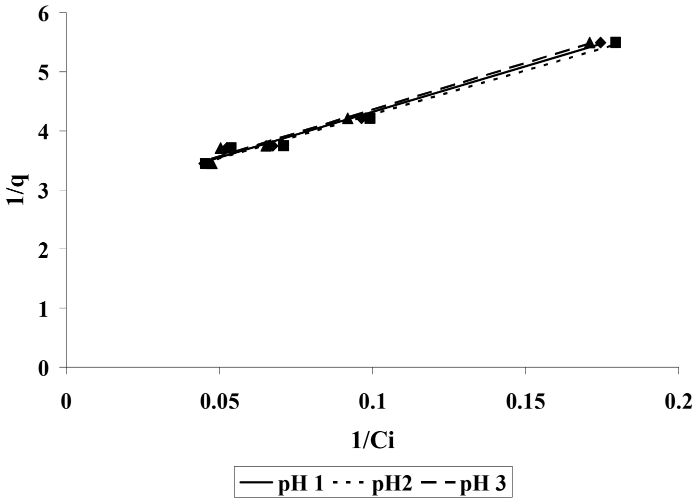

Figure 5.12 Linearized data from the adsorption isotherm constructed using wastewater at pH 1 (♦), pH 2 (■) and pH 3(▲).

In Table 5.7, the calculated parameters from the pure rhodium isotherm are compared to the parameters calculated from the wastewater isotherm. Immediately obvious is that the parameters for the wastewater isotherms are identical at each pH. This may suggest that metal uptake is pH-independent at low pH. However, the parameters from the pure solution show definite pH-dependence, in that the $Q_{\max}$ decreases with an increase in pH.

Table 5.7 A comparison of the calculated parameters from the pure and wastewater isotherms produced.

pH	$Q_{\max}$	*b*	Isotherm
1	7.968	29.668	Rh solution
	0.360	5.543	Wastewater
2	6.993	16.744	Rh solution
	0.360	5.382	Wastewater
3	5.744	10.287	Rh solution
	0.360	5.740	Wastewater

Effect of suspended solids in wastewater on adsorption of rhodium

Figure 5.13 showed that adsorption was better in filtered wastewater than in wastewater still containing the suspended solids fraction, but only by approximately 3 – 4 %. This does not fully explain the 50 % difference in removal efficiency when comparing the pure solution with the wastewater, as observed in the experiment in section 5.5.

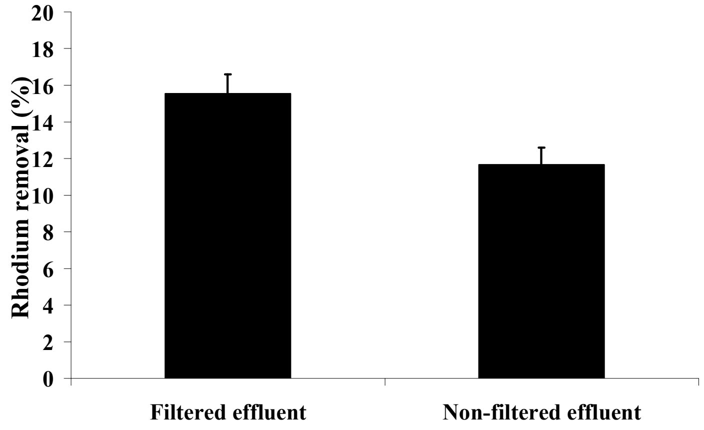

Figure 5.13 A 3 – 4 % increase in adsorption is obtained by filtering the wastewater to remove the suspended solids fraction.

Effect of metal interference on rhodium adsorption from wastewater

The presence of other precious metals in the wastewater as anions may cause the decrease in adsorption of rhodium by increasing the competition for binding sites on the biosorbent. However, when the wastewater was tested for the presence of gold, palladium and platinum, all were found to be present in trace amounts only (Table 5.8).

Table 5.8 Anionic precious metal analysis of wastewater.

Precious metal anion	Metal content (mg/L) ± SD
Gold	0.987 ± 0.185
Palladium	0.190 ± beyond limit of detection
Platinum	0.000 beyond limit of detection

5.6.3 DISCUSSION

The kinetics of adsorption of rhodium from pure solution and from the wastewater seemed to be quite similar. Both achieved equilibrium within the first 30 minutes. However, unlike the 50 % removal equilibrium in the pure solution, equilibrium in the wastewater was at less than 10 % rhodium removal. This is possibly a result of the different chloro-species of rhodium present in the wastewater compared to the single species in the pure solution. It is possible that the maximum extractable rhodium was removed and that the remainder has no affinity for the biosorbent

The wastewater adsorption isotherm behaved very differently to the isotherm obtained using a pure rhodium solution. In Table 5.6 the Langmuir parameters calculated from each isotherm at their respective pH levels are tabulated. Most obvious is that the $Q_{\max}$ (maximum metal uptake mg/g of biosorbent) and the b (affinity of biosorbent for metal) for the wastewater is identical at each pH. This indicates pH independent binding. This may change as the pH is increased further, but this was not examined, as the spontaneous precipitation threshold for pure rhodium is approximately pH 3. These values are also significantly lower than those obtained from the pure rhodium isotherms. Again this may be attributed to the unextractable character of the rhodium in the wastewater.

It was noted early on in the study that a large suspended solid content was present in the wastewater. Until now, all wastewater used has been used with this suspended solid volume intact. It was, therefore necessary to determine whether or not the solids affect the adsorption of rhodium from the wastewater. The difference found (3 – 4 %) is not large enough to implicate the suspended solid fraction of the wastewater in significantly inhibiting rhodium binding to the biosorbent.

Other metal interference was largely ruled out by analysis of the precious metal content of the wastewater. An insignificant amount of residual metal is present due to the high efficiency of the refining and extraction of the PGMs, and as rhodium is the last to be extracted, it is expected that the others would be present in only trace amounts. Base metals should not interfere in binding at such low pH. A large body of work exists detailing the preferred adsorption pH for copper, iron, cobalt and nickel (significant base metal content in this wastewater), all of which are in excess of pH 1.3. Sheng *et al.* (2004) showed that optimal adsorption pH for copper was 5.0, and for nickel was 5.5. Esposito *et al.* (2000) showed a similar result for copper. Results for iron show that this is the only base metal that may interfere, as its optimum adsorption pH was approximately 2 (Aksu and Gülen, 2002; Sa and Kutsal, 1996). Cobalt, investigated by Suhasini *et al.* (1999) showed maximum uptake at pH 7.

5.7 COMPARATIVE COLUMN STUDIES

Volesky (2001) states repeatedly that the most effective configuration for a sorption process is a fixed/packed bed reactor system. However, the performance of the column depends entirely on the efficiency of the packing material at adsorbing the target metals. Packed bed columns were constructed from glass tubes with internal diameters of 2.5 cm. The height of all beds when packed was maintained at 5 cm. The void volume of the column was approximately 15 – 18 cm^3. Figure 5.14 illustrates the packed-bed reactor setup used in this study.

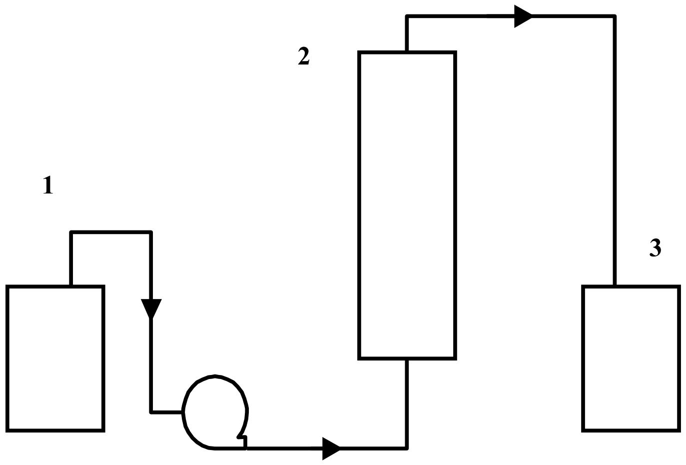

Figure 5.14 Setup of packed bed reactor system. 1. Wastewater reservoir. 2. Packed column. 3. Effluent reservoir.

5.7.1 MATERIALS AND METHODS

Un-neutralised biosorbent columns

A comparative study involving the column setup described was performed with a pure rhodium solution and a wastewater sample. A volume of 1 L was passed through a column with a retention time of 15 minutes (Ismatec pump, Switzerland) (taken from adsorption kinetics experiment, section 5.5). Each column was packed with 9 g of immobilized yeast biomass. Samples were taken every 20 ml for the first 100 ml, then every 100 ml for the remainder of the experiment.

Neutralised biosorbent columns

A second comparative study was performed as described above, however, in this case the alkali residue was completely removed from the biosorbent by soaking in 1 M HCl for 10 minutes, followed by continuous distilled water washes until the pH of the aqueous solution reached approximately pH 3. The biosorbent was then dried at 80 ºC for 6 hours before use.

5.7.2 RESULTS

Biosorption from a pure rhodium solution

In Figure 5.15, the metal removal curve seemed to follow the pH profile quite closely, peaking at 100 ml in response to the pH peak in the corresponding 100 ml. This may suggest that a degree of precipitation took place rather than adsorption, especially as the pH peaked at almost 9. The removal curve rapidly levelled off at approximately 10 % removal after a volume of 400 ml had passed through the column. Of the approximately 60 mg of available rhodium passed through the column, only 16 % (9.78 mg) was adsorbed/precipitated by the column.

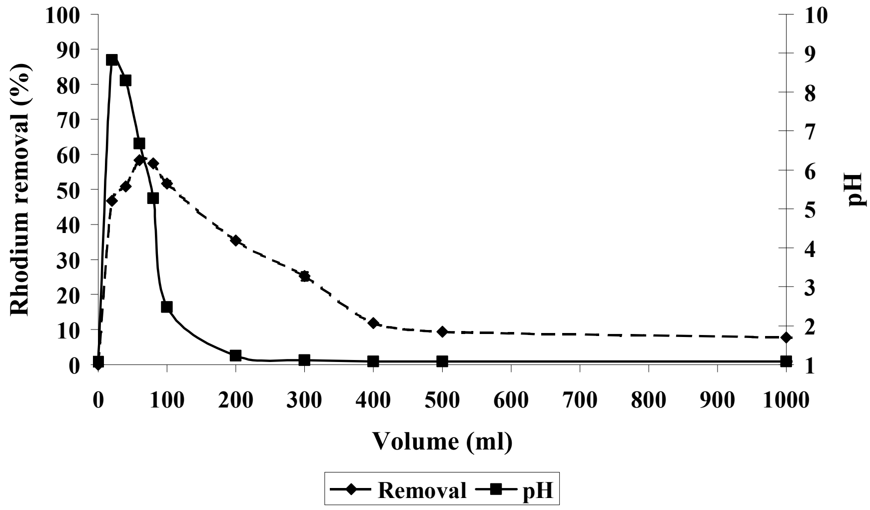

Figure 5.15 Percentage removal of rhodium by un-neutralized biosorbent from a pure rhodium solution in relation to the pH profile.

The column run with neutralized biosorbent showed a dramatically different pattern. Figure 5.16 shows the pure solution removal curve not tracking the pH profile at all, and because the pH did not peak above 3, it can be assumed that no precipitation took place. The percentage removal peaked and remained at above 70 % for the first 500 ml, and after that, showed a slight decline to just above 50 % removal. Of the approximately 50 mg of rhodium passed through the column, 69 % (32.67 mg) was adsorbed to the biosorbent.

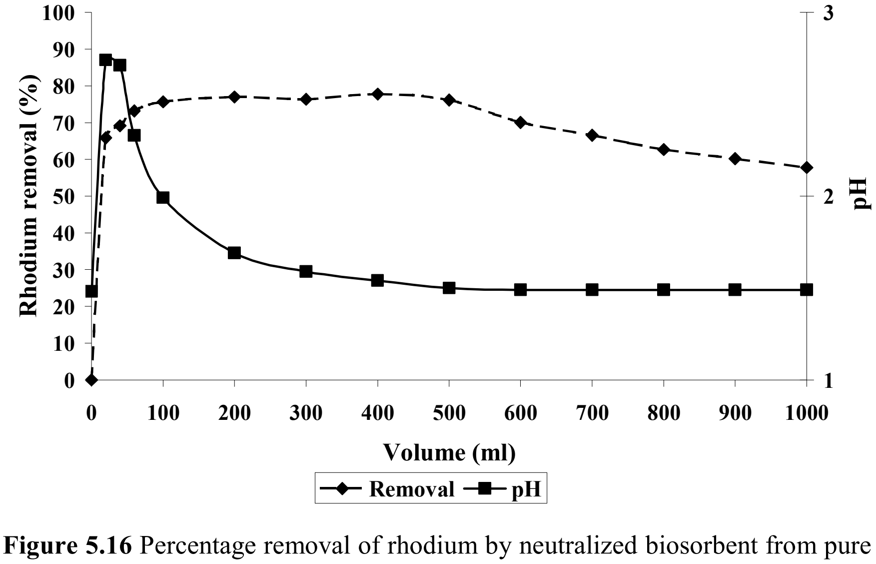

Figure 5.16 Percentage removal of rhodium by neutralized biosorbent from pure rhodium solution in relation to the pH profile.

Biosorption of rhodium from wastewater

In the case of the wastewater column using un-neutralized biosorbent (Figure 5.17), again the pH profile and the removal curve closely followed the same trend. The pH peaked at approximately 8, lower than the pure rhodium column due to the stronger buffering capacity of the wastewater. The removal curve dropped to 0 % by the 400 ml mark and only trace removal was noted after that. Of the approximately 50 mg of rhodium passed through the column, only 4.35 mg was adsorbed or precipitated.

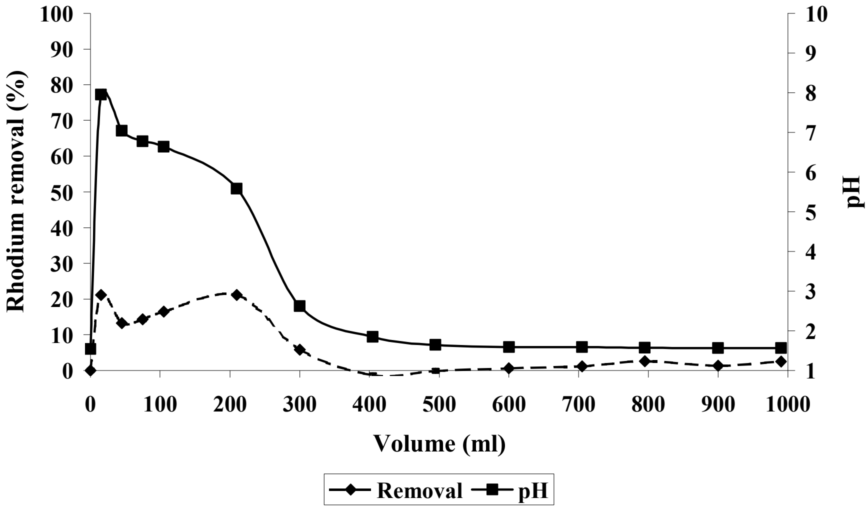

Figure 5.17 Percentage removal of rhodium from wastewater by un-neutralized biosorbent in relation to the pH.

The neutralized column used to remove rhodium from wastewater (Figure 5.18) showed a similar pattern to that of the un-neutralised biosorbent column. The removal curve however, did not peak as sharply in response to the pH increase, and this time, of the approximately 70 mg of rhodium passed through the column, only 3.46 mg adsorbed to the column.

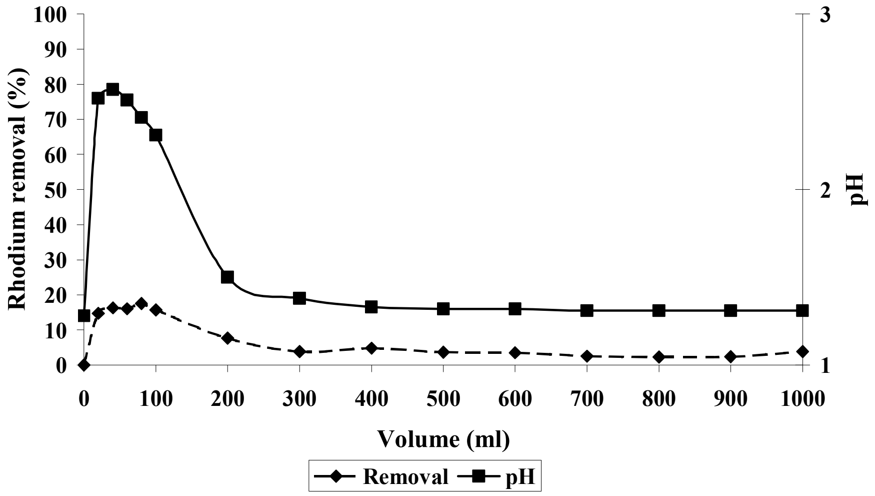

Figure 5.18 Percentage removal of rhodium from wastewater by neutralized biosorbent and the relationship to the pH.

5.7.3 DISCUSSION

The un-neutralized column adsorbed only 16 % of the available rhodium from the pure solution, while the neutralized biosorbent adsorbed more than four times as much (69 %). This is due to the alkali content of the un-neutralized biosorbent, which initially raised the pH of the column effluent to almost 9. At this pH, a small amount of the metal precipitated, but once this alkalinity had been washed out of the column, the biosorbent remained deprotonated (negatively charged), and thus could not bind anionic metal species. Zhao *et al.* (1999) corroborate this suggestion that residual alkali within the biomass pores may influence biomass-accumulation patterns through microprecipitation. They also reported a similar result when removing chromium(VI) from solution using non-viable *Azolla filiculoides*, in which an increase in the pH of the treated solution was noted. Chromium uptake was also lower during this experiment (Zhao and Duncan, 1997).

The neutralized biosorbent column showed a stable and good removal of rhodium. The pH of the effluent did not rise higher than pH 3, which greatly decreased the possibility of microprecipitation and the biosorbent was far more protonated (positively charged). This curve seemed to better represent the adsorption reaction occurring within the packed bed, as most published results follow the same basic trend, i.e. the pH remains approximately stable and does not interfere with the metal biosorption. Other column experiments by Zhao *et al.* (1999) showed similar results, in which the pH value of the effluent was not raised by the biomass, probably due to the fact that the highly acidic solution pH was not affected by changes in the hydroxyl and proton concentrations on the biomass surface.

Both columns challenged with wastewater showed similar trends. The un-neutralized column resulted in a curve similar to the un-neutralized pure solution column, in which the pH peaks resulted in removal peaks (probably precipitation). This pattern was not as obvious in the neutralized column, but both columns removed minimal rhodium. Zhao *et al*. (1999) published a similar trend when treating an electroplating wastewater, where they found that impurities in the wastewater were being adsorbed at the expense of the zinc ions they were targeting. The low rhodium recovery from the wastewater may be attributed to the complex chemistry of rhodium discussed in Chapter 2, and it may be that the columns had adsorbed all of the rhodium that was present in an extractable form. For example, Garnham (1997) cites a number of cases in which the speciation of the metal greatly affects the biosorption capacity of the biosorbent; such as mercury, which under different pH conditions and redox potentials can form HgS_2^{2-}, $Hg(OH)_2$, Hg^0, HgCl(OH), HgCl and Hg^{2+}, and efficient biosorption is dependent on the species present in the solution. This is particularly apparent when comparing the pure solution adsorption with the wastewater adsorption. In the case of the wastewater a number of species of varying extractability exist, while in the pure solution, the dominant, and possibly only, species present is the highly extractable $RhCl_6^{3-}$.

5.8 DESORPTION OF RHODIUM FROM THE BIOSORBENT

The ability to recover metals of value from biosorbents is highly advantageous. In most cases, this is easily achieved using mineral acids such as HCl or HNO_3. However, in many cases, notably the precious metals, chelators and ligands such as thioureas and thiocyanates are far more successful desorbents.

5.8.1 MATERIALS AND METHODS

Triplicate flasks were prepared with 25 ml of an acid at differing molar concentrations (1, 4 and 8 M HCl, 1 and 4 M HNO_3, 1 and 4 M H_2SO_4). Concentrated aqua regia (3:1 HCl: HNO_3) and a solution of 0.3 M thiourea (Merck, South Africa) in 1 M HCl were also tested, as these are often more successful at desorbing precious metals such as gold, platinum and palladium (Godlewska-Żyłkiewicz, 2003). The experiment was initiated by the addition of 0.5 g of rhodium-laden biosorbent. All flasks were agitated at 200 rpm for 1 hour, after which a 3 ml sample was filtered and assayed for metal concentration.

Three further 0.5 g samples of rhodium-laden biosorbent were digested in concentrated nitric acid to determine the approximate metal content. This concentration was treated as 100 %, i.e. all metal desorbed by the acids, etc. was reported as a percentage of this total.

5.8.2 RESULTS

From Figure 5.19, it was concluded that all three concentrations of HCl were ineffective desorbents, the highest concentration, 8 M, capable of desorbing less than 15 % of the bound rhodium. The other acids were more successful, with 4 M HNO_3 being able to desorb just less than 25 % of the bound rhodium. The sulphuric acid results fell between the efficiency of HCl and HNO_3, i.e. both the 1 and 4 M concentrations desorbed more than the 8 M HCl but less than the 4 M HNO_3. The 0.3 M thiourea in 1 M HCl desorbed with the same efficiency as the H_2SO_4 treatments, but with more variability. The aqua regia treatment desorbed by far the most rhodium from the biosorbent, more than 50 % in fact. However, the biomass was almost completely digested by the acid combination, possibly allowing more rhodium to resolubilize than if the biosorbent had not degraded to such an extent.

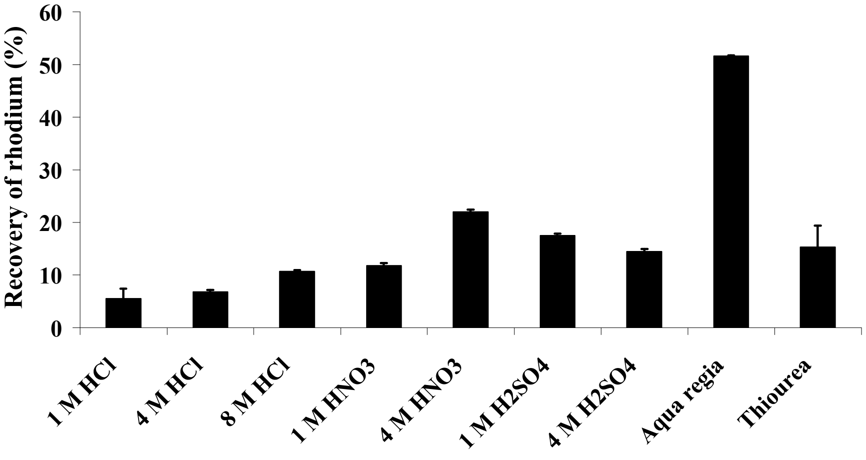

Figure 5.19 Desorption of rhodium from metal-laden yeast biomass.

In Table 5.9, the eluate: feed concentration ratios are tabulated. Ratios approaching 1 are preferred as this translates to desorption approaching 100 %. The aqua regia ratio was the highest (0.366), followed by the 4 M H_2SO_4 (0.220). All of the other desorbent ratios were far below that, implying inefficiency when used as a desorbent for rhodium.

Table 5.9 Eluate: feed concentration ratios.

Eluant	Ratio (desorbed/adsorbed)
1 M HCl	0.054
4 M HCl	0.068
8 M HCl	0.107
1 M HNO_3	0.118
4 M HNO_3	0.220
1 M H_2SO_4	0.175
4 M H_2SO_4	0.144
Aqua regia	0.366
Thiourea	0.109

5.8.3 DISCUSSION

When the application of a packed-bed reactor configuration for a continuous biosorption process is considered, the overall efficiency of the system is evaluated using a ratio of eluate metal concentration to feed metal concentration (Jalali *et al.*, 2002). The results of this experiment showed that mineral acids were not the optimal eluant for the recovery of rhodium from the biomass. Generally, mineral acids are used to desorb base metals, in which only a change in pH is required to break the bond between the metal ion and the biosorbent. This desorption usually requires a 1 M concentration or less. Jalali *et al*. (2002) recovered lead adsorbed on Sargassum biomass using 0.1 M HNO_3, Wilhelmi and Duncan (1995, 1996) eluted copper, zinc, cobalt, cadmium, nickel and chromium from immobilized yeast using 0.1 M HCl and a 0.1 M H_2SO_4 solution was used by Volesky (1990) to elute chromium from a microbial biomass. Aqua regia (3:1 HCl: HNO3) achieved the largest apparent desorption, however, the biosorbent was partially hydrolysed by the strong acid, and as such, the further use of aqua regia was not considered.

Acidic thiourea has been used as an eluant for a number of anionic metals including gold (Bedell and Darnall, 1990), palladium and platinum (Godlewska-Zyłkiewicz, 2003), and although the thiourea treatment result was poor, higher desorption could be obtained by adjusting the concentration of the solution. Investigation of other metal chelators and ligands may yield a highly efficient rhodium desorbent, e.g. thiourea and ferric ammonium sulphate (gold elution), $CaCl_2$ (cobalt elution) (Volesky, 1990) or EDTA (copper, cobalt and cadmium elution) (Brady and Duncan, 1994). The problem, however, lies in the strong bond formed between the chelator/ligand and the metal. This bond could make the recovery of a pure metal solution much more difficult. It would also generate a further wastewater solution that may even be more toxic to the environment than the metal-laden wastewater to be treated initially.

5.9 SUMMARY AND CONCLUSIONS

Saccharomyces cerevisiae biomass was immobilized using polyethylenimine and glutaraldehyde and then treated with hot alkali. This process produced granules of variable size, but good chemical and physical resistance. Fully immobilized biomass exhibited a far higher removal capacity that heat-inactivated biomass, 70 % versus 45 %, respectively. This was due to the removal of extraneous proteins by the alkali treatment, which improved availability of binding sites on the biomass. The average percent yield for the formulation process was 20 %. This was higher than the yield reported by Stoll (1996), 15 – 17 %, using the same immobilization procedure. The area of greatest weight loss was the alkali treatment, in which a large proportion of lipids and proteins were lost. A major advantage of the alkali treatment is the removal of autolytic enzymes, thereby increasing the shelf life of the biosorbent. Variations in removal efficiency were noted between biosorbent batches. This was the major drawback when scaling up the biosorbent production process. These variations were attributed to the variable granule sizes produced, as a batch with a higher small granule content adsorbed more rhodium than a batch with a low small granule content. It was found that granule sizes of less than 2 mm diameter were capable of 20 % greater uptake than granules of more than 2 mm diameter.

The adsorption kinetics of the pure rhodium solution indicated a rapid uptake of less than 20 minutes before solution equilibrium was reached. This is a major indicator of passive adsorption to the cell surface, i.e. biosorption. The rapid uptake is common in biosorption processes, where it is considered advantageous as it allows for shorter residence times within smaller reactors, conferring both cost and capacity benefits. The calculated isotherm parameters indicated that pH 2 was optimal for rhodium uptake by the biosorbent. The $Q_{\max}$ value was relatively low, 6.99 mg/g, and the affinity coefficient, b, was high, 16.75, which may indicate the need for further, or different pre-treatment of the biosorbent to enhance the uptake of rhodium. The pH optimum (pH 2) was similar to experimentally determined optima for a number of other anionic metals in solution.

The removal of rhodium from the wastewater was not as efficient as from the pure solution; only 20 % of the rhodium was removed from wastewater compared to 75 % from the pure solution. Interference by suspended solids has been found to inhibit metal ion binding, but in this case, the suspended solids fraction was responsible for minimal inhibition (3 – 4 %). Competitive interference by other precious metals in the wastewater was also ruled out, as the precious metal content (other than rhodium) was insignificant. There was a small base metal content in the wastewater, but published data regarding the pH optima for uptake of these metals suggested that at such low pH, they would not bind to the biosorbent.

There was a similarly rapid adsorption of rhodium from the wastewater, with equilibrium reached within 20 minutes, but again the removal efficiency was very low, with equilibrium established at 10 % removal. The results from the isotherm study seemed to suggest pH-independent binding at low pH, as the calculated values of $Q_{\max}$ and b were identical at all pH values investigated ($Q_{\max} = 0.36$ mg/g and $b = 5.5$). These were also much lower than those of the pure solution, and as possible inhibitors such as suspended solids and precious and base metals had been discounted, it could be suggested that the much lower and less efficient recovery was possibly due to the chemistry of the rhodium chloro-complexes in the wastewater. It is possible that all of the readily extractable metal had been removed and that the remainder is present in a form that is not amenable to this type of extraction.

In the column experiments with pure rhodium, the neutralized biosorbent extracted rhodium with 69 % efficiency, and the un-neutralized extracted with only 16 % efficiency. The lower efficiency of the un-neutralized column was due to the high residual alkali content, which raised the pH of the wastewater and initiated precipitation of the metal. Once the alkali had been washed from the column, the biosorbent remained deprotonated and presented very few binding sites for the anionic rhodium ions. The neutralized column, on the other hand, provided sufficient binding sites for sustained removal from the first 500 ml, after which a small decrease in removal was noted. In the wastewater experiments, the alkali present in the un-neutralized biosorbent again produced a pH peak resulting in precipitation of the rhodium, with minimal adsorption after the alkali had washed out. The neutralized column results, however, did not look very different from the un-neutralized column results, as very little rhodium was adsorbed from in either experiment. Again, this may be caused by the species of rhodium present in the wastewater not being in extractable form.

Efficient desorption of bound metal ions is imperative in a continuous packed-bed adsorption operation. The overall efficiency of the process is usually determined by assessing the eluate: feed concentration ratio of the metal, i.e. concentration desorbed versus concentration adsorbed. Of the desorbents tested, aqua regia proved to be the strongest. It also hydrolysed the biosorbent, making it unsuitable for use as a desorbent in a continuous process. Mineral acids were unable to elute rhodium with any efficiency and have also proven ineffective with gold, platinum and palladium. A combination of a complexing ligand and a decrease in pH (such as thiourea in HCl) has been efficient in desorbing gold, platinum and palladium, and may be effective in the case of rhodium after optimization of the concentrations needed to desorb the bound rhodium.

Rhodium ions have proved to be amenable to extraction via biosorption. The chemistry of the wastewater has, however, become the greatest obstacle to the success of the process. Further pre-treatment of both wastewater and biosorbent are necessary in order for this process to be maximally efficient. The wastewater must be treated, either by addition of a suitable catalyst or by heating, to convert the rhodium species present into extractable species. The biosorbent must also be further developed, possibly by acid treatment rather that alkali treatment, to enhance the availability of binding sites for adsorption of rhodium. If these refinements are successful, the resultant biosorption process would be a viable alternative to the present recovery processes used at precious metal refineries.

CHAPTER 6

GENERAL DISCUSSION

6.1 WASTEWATER CHARACTERIZATION

In order to select the best treatment technology for a particular wastewater, it is necessary to determine the physical, chemical and biological characteristics of the wastewater. These parameters will guide the method selection process, as many technologies exist, and all may be tailored to meet the specific treatment requirements determined during the wastewater characterization.

In the present study, remediation of the wastewater is of secondary importance to the recovery of valuable rhodium metal dissolved in the wastewater. In spite of its secondary importance, the wastewater was still characterized and compared to Department of Water Affairs and Forestry (1996) guidelines for industrial water reuse (Category 4). If a wastewater can be treated to meet these guidelines, it may be used in tasks such as ash quenching, dust suppression, transport, fire fighting, irrigation and rough washing. Characterization of the wastewater showed that the ammonia (14.18 g/L), chloride (44.17 g/L), sulphate (5.67 g/L) and COD (26.68 g/L) concentrations were far in excess of the acceptable limits, as was the suspended solids concentration (44.9 mg/L). The pH was extremely low (1.2 – 1.5) and the acidity was very high (3.67 $gCaCO_3/L$). As expected, there were only trace concentrations of PGMs (excluding rhodium (65 – 70 mg/L)), and all of the base metals investigated were at or below the guideline upper limit. There was a very high concentration of sodium in the wastewater, which together with the high chloride concentration results in an extremely high ionic strength wastewater. Overall, the wastewater did not conform to the guidelines and the reuse of this wastewater without pre-treatment may result in a number of problems, such as corrosion of pipes, scaling and fouling, blockages and the production of sediments.

The high acidity concentration measured in the wastewater provides a significant pH buffering capacity. This was illustrated when the precipitation of rhodium was compared from a pure solution and from the wastewater (Figure 2.6). It took more alkaline reagent to precipitate rhodium from the wastewater than from the pure solution. This may be an advantage or a disadvantage depending on the process chosen for the recovery of rhodium. It would seem to be a disadvantage in the current metal removal process, as the non-selective precipitation of metals from the wastewater would require a large dose of alkali in order to overcome the acidity. However, in processes such as fluidized-bed nucleated precipitation (Chapter 4), this slow precipitation may be advantageous in that lower doses will initiate the precipitation of a small amount of the rhodium, which should be sufficient to begin the nucleation and growth of precipitated rhodium crystals on the sand grains.

6.2 THE SULPHIDE-EXTRACTION MEMBRANE BIOREACTOR (SEMB)

Three technologies were selected for as possible processes for the recovery of rhodium from the wastewater. The first, the SEMB, is a membrane coupled to a sulphidogenic bioreactor. The SEMB recovers metal ions via precipitation with biogenic sulphide. A silicone membrane separates the wastewater from the SRP, allowing H_2S to permeate from the biomedium phase into the wastewater and so precipitate the metal. Charged species in the wastewater cannot permeate the membrane, making it possible to pass highly inhibitory wastewaters such as this through the tubes without inhibiting the SRP.

For optimal mass transfer of H_2S through the membrane, the sulphide must be in the dissolved gas form, which dominates at low pH. As such, the ambient pH conditions required that optimizations take place in order to maximize sulphide mass transfer across the membrane. The SRP supernatant pH was dropped from approximately 8 to 3, and in the initial experiments, the receiving solution (water) was adjusted to pH 3. These optimizations resulted in a maximum sulphide mass transfer of 1.04×10^{-5} m/s. This figure represents a ten-fold increase over the mass transfer at ambient pH. The results achieved were comparable with the data published by Chuichulcherm *et al.* (2001). With much thinner membranes, their highest recorded mass transfer was 9.91×10^{-6} m/s. The pH-optimized system was then challenged with various metal solutions. The first, a 250 mg/L zinc(II) solution reacted well and within 24 hours, more than 90 % of the zinc had precipitated as zinc sulphide. Again this data agreed with that published by Chuichulcherm *et al.* (2001). A copper solution was also introduced into the membrane, but the results were very different from those achieved with zinc. A copper sulphide precipitate film formed on the membrane surface, blocking any further transfer of sulphide. Only a small percentage of the copper was precipitated from solution. A similar result was achieved when a rhodium solution was used. Again, a metal sulphide precipitate film fouled the membrane and allowed no further transfer of sulphide into the metal stream. The copper and rhodium solutions may have reacted similarly due to the similarity in their chemistry according to the hard and soft acid and base (HSAB) theory discussed in Chapter 2. All three metals are classified as borderline acids according to Pearson (1966), but according to the Ahrland *et al*. (1958) classification, zinc(II) shows class *a* character, copper(II) shows borderline character and rhodium(III) shows class *b* character. These classifications are broadly analogous to the hard and soft classifications, in which class *a* is hard and *b* is soft. Thus, if copper is a borderline tending to class *b* metal, which can be assumed due to the pronounced class *b* character of copper(I), similar reactions could be expected from both copper and rhodium to the SEMB treatment.

The Ahrland *et al*. (1958) classification criteria state that class *a* acceptors prefer to bind with the first ligand atom in each periodic group, i.e. N, O, and F, while class *b* acceptors prefer the second or subsequent atoms, i.e. P, S, and Cl. In this case, all three metals tested bound with the sulphide ions and precipitated, but they did so in such a way that the separation according to Ahrland *et al.* (1958) was apparent, i.e. zinc, the only definite class *a* acceptor bound and formed a crystalline precipitate, while copper and rhodium, borderline/class *b* acceptors, formed amorphous precipitates which adhered to and fouled the membrane.

In terms of HSAB theory, all three metals are classified as borderline acids, while the sulphide ion is a soft base. The fact that these metals bound to the sulphide ions and precipitated out of solution shows the approximate nature of the classification, in that despite characteristics such as polarizability predicting that soft binds to soft, hard to hard and borderline to borderline, acids and bases still bind outside of their categories if the circumstances are such that the bonding is favoured, e.g. metal in a solution saturated with sulphide ions.

The precipitate film formed by copper and rhodium could not be removed via non-destructive methods. Recovery of the precipitate was only possible using destructive physical methods. This means that each membrane would only be used for a single treatment cycle before it would need to be destroyed and replaced. This adds a large operating cost to the application of this process, which does not in any way lend an advantage to the system efficiency.

Up until this stage, all experiments had been performed using supernatant from a separate sulphidogenic bioreactor. For the wastewater trial, a bioreactor was set up and the membrane was submerged inside it. The bioreactor was monitored for four weeks before the wastewater was introduced into the membrane loop. Throughout the six-week experiment, the ammonia and chloride concentrations were monitored within the bioreactor. This was done in order to determine whether any counter transfer of chlorinated organic compounds occurred. The bioreactor showed no significant increase in these concentrations after the wastewater was introduced into the membrane loop, indicating that no counter transfer was taking place from the wastewater to the bioreactor.

Within 48 hours of introduction of the wastewater, a precipitate film had formed only the membrane and a precipitate was visible in the wastewater reservoir. From the results obtained using the pure rhodium solution, showing that the rhodium ions, at similar concentration to that found in the wastewater, completely fouled the membrane, it can be suggested that in the case of the wastewater trial, the rhodium ions may be almost solely responsible for the fouling. The film on the membrane not only slowed the transfer of H_2S, but also adversely affected the SRP within the bioreactor by causing an H_2S build up, which slowed the reduction of sulphate, thus depressing the cellular respiration of the consortium. After the initial 48 hours in which the precipitate formed, the wastewater maintained a stable, low concentration of sulphide. No further influx from the bioreactor was possible, and no sulphide was leaving the wastewater solution as sulphide precipitate. This seemed to suggest that all precipitable ions within the wastewater were precipitated in those first 48 hours. Analysis of the precipitate showed that less than 1 % consisted of PGM precipitate, with rhodium being present in the largest proportion. The remaining 99 % consisted of base metallic and non-metallic ion precipitates. This suggested that the SEMB might not be capable of selective precipitation from wastewater, as all ions capable of forming sulphide precipitates were precipitated from the wastewater.

The behaviour of the rhodium ions in the wastewater mirrored that of the rhodium in pure solution, i.e. the membrane was fouled in both cases within a short period of time. This indicates that despite the differences in species composition between the pure solution (single species, $RhCl_6^{3-}$) and the wastewater (numerous species in varying states of aquation), the rhodium ions reacted in the same way to the sulphide ions, producing an amorphous precipitate capable of forming a film on the membrane through which no further sulphide ions could pass. This film formation becomes a major factor in the non-selection of this technology for the effective recovery of rhodium ions from the wastewater in that the precipitate, as well as preventing the total precipitation of all of the rhodium in solution, can only be recovered by destroying the membrane. This is a system complication that would require a significant increase in operating costs, as the membrane would need to be replaced directly after the precipitate film forms.

6.3 NUCLEATED PRECIPITATION IN A FLUIDIZED BED REACTOR (FBR)

The second technology screened as a method for the recovery of rhodium from the refinery wastewater involved the initiation of nucleated precipitation, via the addition of sodium carbonate, of the metal ions onto inert media within a fluidized bed reactor.

The optimal molar ratio of carbonate ions to metal ions is an important parameter in this technology, as it is this parameter that controls the degree of pH adjustment applied to the wastewater. The optimal ratio will initiate precipitation, although not rapidly enough to produce discrete precipitation, at a rate that favours nucleated precipitation. Although no significant difference in precipitation efficiency was found for all ratios tested from 1/1 to 4/1, a ratio of 2/1 was chosen as optimal according to published data regarding this technology (Lee *et al.*, 2004; Zhou *et al.*, 1999). A decrease in precipitation efficiency was noted at a 6/1 ratio. This was baffling, as a ratio greater than 2/1 was thought to induce rapid, usually discrete precipitation.

The optimum sand concentration was again chosen according to published literature (Zhou *et al.*, 1999). A concentration of 200 g/L showed a relatively stable adsorption curve, although these data were later proved to be inconclusive as it was shown that rhodium exhibits no adsorption affinity towards the sand grains. The adsorption isotherms produced showed conclusively that no simple adsorption process takes place between the rhodium ions and the sand grains. This implies that the nucleation process can only be initiated by the precipitation of rhodium.

The FBR experiments indicated that the 2/1 ratio suggested by Zhou *et al*. (1999) and Lee *et al*. (2004) was insufficient to initiate precipitation of the rhodium from the wastewater. As discussed in Chapter 2, this is most likely due to the buffering capacity of the wastewater. A larger dose of alkali reagent may be necessary in order to overcome this acidity. The 2/1 carbonate/metal ratio is primarily required to raise the pH of the wastewater enough to initiate precipitation. In the present case, the pH was not raised by even a single pH unit, unlike the experiments conducted by Zhou *et al*. (1999), in which the same 2/1 ratio was sufficient to raise the pH of the zinc solution to greater than 9, and in the experiments performed by Lee *et al*. (2004), in which the 2/1 ratio raised the pH of a copper solution to more than 8.

However, if this system had worked, a number of predictions could be made regarding it effectivity based on the characteristics of rhodium reviewed in Chapter 2. Firstly, both the carbonate and hydroxide ions are characterized as hard bases, preferring not to bind to borderline or soft acids such as rhodium. As these ions are known to be responsible for the precipitation reaction occurring in this FBR system, the implication is that for the bonding to occur, the aqueous environment would need to be saturated with either carbonate or hydroxide ions, giving the rhodium little alternative but to bind to these hard bases. A similar implication lies in the Ahrland *et al.* (1958) classification, in which rhodium ions would not preferably bind to the first ligand in a periodic group, e.g. O in OH^- and CO_3^{2-}. Saturation of the wastewater environment with these precipitation-inducing ions would also induce the precipitation of the other metals and non-metals present, resulting in an impure precipitate, requiring further refining and purification.

6.4 IMMOBILIZED YEAST BIOSORBENT

The third, and most well established technology screened for rhodium recovery capacity was a simple biosorption process. Yeast biomass (*Saccharomyces cerevisiae*) was immobilized by cross-linking with glutaraldehyde and polyethylenimine. The fully immobilized biosorbent was capable of 30 % higher adsorption than heat-treated native yeast. This improved availability of binding sites was due to the removal of superfluous lipids and proteins during the alkali treatment. The granules produced exhibited good mechanical strength and resistance to dilute acids, but were of variable size. This size variation proved to be responsible for variations in the efficiency of the biosorbent from batch to batch. It was found that granules with a diameter less than 2 mm were capable of up to 20 % higher removal than the granules with a diameter larger than 2 mm. According to Volesky (2001) a good biosorbent for application to a packed bed reactor should be between 0.7 and 1.5 mm in diameter in order to achieve a porous bed with minimal resistance to flow but maximal mass transfer onto the granules.

The rapid uptake rate of rhodium ions onto the biosorbent is a both a common and advantageous result in that the shorter contact time allows for smaller process equipment and a more rapid flow-through of wastewater, resulting in significant cost benefits. The adsorption kinetics of rhodium in the wastewater was similarly rapid, but much lower equilibrium removal efficiency was recorded (< 10 % vs. 50 % in pure solution). This result was the first indication of the importance of the species composition of the rhodium ions present in the wastewater. The adsorption isotherm produced using the wastewater was also significantly different to that produced with a pure rhodium solution. The pure solution isotherm indicated pH dependent binding, with Qmax decreasing with increasing pH. In the wastewater isotherm, no dependence on pH was indicated. This may be due, in some way, to the acidity of the wastewater providing a low pH buffering capacity which could decrease the reactivity of the rhodium ions to small increases in pH (such as simple unit changes). Again, the removal efficiency was very low due to the very low proportion of extractable rhodium species present in the wastewater. Other potential interference from wastewater components such as the suspended solids fraction and other metals were ruled out. Removal of the suspended solids fraction resulted in a negligible 3 to 4 % increase in adsorption, no competing PGMs were present in the wastewater to inhibit binding, and the base metal components were not expected to provide any competitive interference at such a low pH.

Packed bed biosorption studies indicated that residual alkali should be removed from the biosorbent, either by neutralization or by acidification. The neutralized biosorbent was capable of removing 50 % more rhodium from a pure solution than the un-neutralized biosorbent. The results from the wastewater columns are harder to interpret, as there seems to be only a small amount of extractable rhodium present. In the un-neutralized column, it is possible that the majority of this extractable rhodium was precipitated, while in the neutralized column it would have been adsorbed.

Efficient desorption of bound metal ions is imperative if a continuous and sustainable biosorption process is required. In the case of most base metals, a simple pH adjustment is sufficient to completely desorb metal ions from the biosorbent. This is usually achieved using a dilute mineral acid. However, mineral acids are known to be ineffective desorbents of precious metals such as gold and platinum. They also proved ineffective at desorbing rhodium from the yeast biosorbent. The addition of a chelating ligand combined with a pH change is often more successful when desorbing precious metals. Acidic thiourea is an example of an effective desorbent of gold and despite the poor results obtained in this case; optimization of the desorbent concentration may result in effective stripping of the rhodium from the biosorbent. What must be considered, however, is that stripping the rhodium into a solution containing such a strong ligand may result in further problems when separation of the rhodium from the ligand is necessary. Also, another wastewater stream is created, which may prove to be more toxic and recalcitrant that the original. A simple solution may be to adsorb the metal to the biosorbent and then incinerate the metal-laden sorbent in a smelter, thereby reintroducing the rhodium into the refining process.

The results obtained from the biosorption experiments supported the literature regarding rhodium chemistry reviewed in Chapter 2. The pure rhodium solution was prepared freshly each day from a standard solution with a high chloride concentration, and it can be assumed that the rhodium existed in the $RhCl_6^{3-}$ form and was thus highly extractable. As the wastewater used in the experiments was high in chloride concentration but, more importantly, was at least 6 to 8 months old, the rhodium complexes could be assumed to be highly aquated and thus in a form not amenable to extraction in this way. Further, if the HSAB theory holds true in this instance, the rhodium ions are covalently binding to cell surface moieties such as phosphoryls, sulphydryls and bonding ionically to other negatively charged groups such as amines and carboxyls.

Overall, the results from each technology indicated that further detailed optimization is required before any of these technologies can be effectively applied in the recovery of rhodium from the wastewater. Three issues have become apparent regarding the wastewater that diminishes the effectiveness of all of the technologies. These include the complex speciation chemistry of the rhodium ions hampering extraction via biosorption, the efficient buffering capacity of the wastewater minimising the effectiveness of the precipitation method, and the form of the precipitate produced via sulphide precipitation. All of these are hindrances present in the character of the wastewater, and must be dealt with effectively before efficient recovery of the rhodium is possible using any technology.

CHAPTER 7

CONCLUSIONS

The wastewater from which rhodium must be recovered has been characterized as extremely harsh in terms of inorganic content. A number of these characteristics result in the recalcitrance of the wastewater towards effective rhodium recovery. The rhodium species present, in particular, have hampered their recovery from the wastewater in a number of ways, with each technology experiencing a problem specific to that technology.

7.1 THE SEMB SYSTEM

The SEMB system generally shows promise as a continuous and sustainable metal recovery process. As long as the SRP are provided with carbon and sulphate sources, hydrogen sulphide will be produced and used in the precipitation of metal ions and the extremely harsh environment within the wastewater will not impede the SRP in any way. It is also a relatively small footprint technology, requiring a single bioreactor in which the membrane is submerged. The rapid wastewater flow-through also means that the bioreactor itself can be quite compact.

When screened in the present study, the SEMB process yielded excellent results when challenged with a zinc solution, precipitating more than 90 % within 24 hours. When a copper solution was substituted for the zinc solution however, the copper sulphide precipitate formed a film layer on the membrane, which obstructed any further sulphide transfer into the metal solution. A similar situation occurred when a pure rhodium solution was used, and only destructive mechanical cleaning effectively removed the sulphide precipitate layer. The rhodium present in the wastewater reacted in the same way as the pure solution and fouled the membrane with an amorphous precipitate composed of all compounds present in the wastewater capable of precipitating as a sulphide.

There are disadvantages apparent in the application of the SEMB technology in the recovery of rhodium from the wastewater, and possibly in its application for removal of various other metals. The metal sulphide precipitate, if not in a crystalline form, will foul the membrane and prevent any further precipitation. If this situation does occur, the fouling is such that only destructive mechanical removal of the precipitate is effective. Hence, the membrane becomes a single-use component of the system, adding greatly to the operating costs involved in running such a system. The system also exhibited non-specific precipitation characteristics, which may impede the separation and purification of the target metal, further adding to costs in the form of additional downstream processing.

In the case of the recovery of rhodium from refinery wastewater, it can be concluded that due to the rhodium sulphide chemistry being such that the precipitate irreversibly fouls the membrane, resulting in the need for destructive force in order to remove the precipitate, the system is not readily applicable. The added disadvantage inherent in the general, non-specific precipitation of all ions present in the wastewater further emphasises the conclusion that an alternative technology should be identified for the purpose of selective rhodium recovery from the refinery wastewater.

7.2 THE NUCLEATED PRECIPITATION FBR SYSTEM

Nucleated precipitation is a simple and well-documented process, generally involving the addition of a seeding reagent to a wastewater in the presence of an inert support media such as sand, resulting in the nucleation, and subsequent precipitation, of metal ions in the solution. Acid washing of the support media usually results in a metal-rich acid effluent and regenerated support media capable of multiple reuse cycles. The nucleated precipitation fluidized bed reactor combines the reaction and settling tanks of the conventional precipitation process. The combination of these two separate environments into a single reactor greatly reduces the space required when installing a new process into an already operational plant. The precipitation reaction is usually initiated when the solution reaches a pH at which the metal salt is no longer soluble. It has been found with base metals, which are soluble at slightly acidic to neutral pH, that the optimal pH for the initiation of nucleated precipitation is > 8. For precious metals, the required pH may be much lower as most precious metal ions are only soluble in very acidic solutions (< 3). With regard to the rhodium wastewater, the suggested carbonate/metal molar ratio of 2 was not able to raise the pH of the wastewater by more than half a pH unit. Thus no precipitation took place and the apparent removal of rhodium shown in Figure 4.8 is in fact merely a dilution effect. The inability of the carbonate solution to raise the pH was due to the large acid buffering capacity present in the wastewater i.e. in the initial wastewater characterization, the acidity of the wastewater was calculated to be 3.67 g $CaCO_3$/L, which translates to a significant ability to resist changes to the pH of the wastewater.

Despite the advantages apparent in the nucleated precipitation FBR, a number of factors have been noted which override those advantages when the system is applied to the rhodium wastewater. The major disadvantage is the large buffering capacity of the wastewater, which implies that a large dose of alkali reagent relative to that used for the base metal examples (Zhou *et al*., 1999; Lee *et al*., 2004) is required in order to initiate precipitation. This impacts negatively on operating costs. A second disadvantage is the lack of selective precipitation of rhodium as there is no control over which metals precipitate, and at which stage they precipitate. This non-selectve precipitation and the need to regenerate the support media contribute to further downstream processing complications, as a separate system would need to be implemented for the regeneration step, and the metal-rich effluent would require a second cycle of refining.

The conclusions that have been drawn from the experimental study regarding the application of the nucleated precipitation FBR to the wastewater cannot however, be taken to mean that this technology is completely unsuitable for the purpose, as the apparent inefficiency may be reversed with further optimization of the system. For example, optimization of the carbonate/metal ratio, to a level at which the buffering capacity is overcome, will result in the initiation of precipitation of the metal ions. However, the non-specific nature of the precipitation may not be reversed.

7.3 THE IMMOBILIZED YEAST BIOSORPTION SYSTEM

Biosorption has, for a long time, been recognized as a viable alternative technology for the removal of metals from industrial wastewaters and natural waters. A wide variety of organisms, both living and non-living, have been found to be capable of sequestering trace concentrations of metals from dilute aqueous solutions. The type and form of the biosorbent used in this study conferred a number of advantages on the overall system operation. The fact that yeast can be obtained as a waste biomass from other industrial processes, and that its use in a non-living form requires no nutrient addition or controlled culture conditions allows for significant cost savings compared to the use of a living biosorbent. The immobilization of the non-viable yeast stabilizes the granules so that their use in a packed bed reactor is not hampered by the mechanical and chemical weaknesses exhibited by non-immobilized biomass. Pretreatment of the biosorbent can also be advantageous if the pretreatment increases the selectivity of the biosorbent for the target metal. The immobilized non-viable yeast biosorbent proved highly efficient in the recovery of rhodium from pure solutions where a single species, the highly extractable $RhCl_6^{3-}$, was dominant. However, when faced with the wastewater, the efficiency of the biosorbent dropped by 50 %. This was not caused by competitive interference by other precious or base metals present in the wastewater, nor was it caused by the suspended solids fraction clogging the biosorbent surface. It seemed that although there was a significant chloride concentration in the wastewater, the age of the solution played a role in aquating the rhodium chloro-complexes, resulting in the formation of unextractable species in the wastewater, as discussed in Chapter 2. The dominant species in the wastewater seem to be far less amenable to extraction based on an ion exchange mechanism, possibly because of the large size of the molecules themselves producing stearic interference, in which only a few molecules can adsorb to the biosorbent surface before the available space is depleted.

The application of the immobilized yeast biosorption system to the recovery or rhodium from the wastewater is hampered by the rhodium species present in the wastewater being in unextractable form. In order to convert the ions into a form amenable to extraction, pretreatment of the wastewater is necessary, either by heating or the addition of a catalyst (as suggested in Chapter 2). This may significantly increase operating costs either by the need to heat large volumes of wastewater or by adding the cost of catalyst reagents to the operating cost of the system. No efficient desorbent was identified in the experimental process, which has significant implications for the downstream processing of the metal-laden biosorbent. Full recovery of the rhodium may be possible only by returning the laden biosorbent to the refinery smelters, in which the carbon-based biosorbent will be completely destroyed, leaving the metal ions to pass through the refining process for a second time. This option allows for only a single cycle of adsorption to the biosorbent before a new batch must be prepared and used. Again, this adds operational costs and increases the volume to be processed by the smelters.

In terms of the current study, it can be concluded that the biosorbent is effective for the recovery of rhodium from pure solutions, but this efficiency is significantly affected by the variety of species of rhodium present in the wastewater. If pretreatment steps were implemented that converted these unextractable rhodium species to the more extractable forms, i.e. less aquated, the process may regain the efficiency experienced when challenged with $RhCl_6^{3-}$ in the pure solution.

CHAPTER 8

FURTHER RECOMMENDATIONS

It has been concluded that only the biosorption system using immobilized non-viable yeast as a biosorbent was suitable for application to this situation. However, the system requires detailed optimization and analysis before it can be implemented. Based on the work conducted in this study, the following recommendations are offered:

1. Suggested system optimizations include a complete physicochemical characterization of the target wastewater, specifically regarding the content and species of the target metal. Once these data are available it will be possible to investigate methods for the conversion of all species present to a species amenable to extraction.

2. The choice of biosorbent and the preparation method used in its immobilization also require optimization. Thus far, commercially available bakers yeast has been used, but for this system to be as cost-effective as possible, a source of waste yeast biomass must be identified. Other biomass preparation methods must be investigated to determine whether the uptake efficiency of the biosobent can be increased. Other methods include heat, acid, surfactant and ethanol treatment, all of which have been shown to increase the uptake efficiency of yeast biomass. Living biomass can also be immobilized, and this factor must be investigated in order to conclude that non-viable biomass is indeed that best option.

3. Once these fundamental optimizations have been achieved, the metal binding characteristics of the biosorbent with the highest binding capacity should be determined. The optimization of system parameters such as pH, temperature and contact time required will positively impact on those characteristics. Those paramters must also be optimized in order to maximize the metal loading capacity onto the biosorbent. These optimizations should also negate any competition or inhibition effects caused by metallic and non-metallic ions present in the wastewater as far as possible.

4. Other analyses required include issues of process design, i.e. batch versus continuous treatment modes and process control parameters, downstream processing optimizations, i.e. incineration versus desorption from the bosorbent, scale-up analysis and an overall cost-benefit analysis.

In truth, while the system showed great promise in recovering rhodium ions, much optimization is required before the system is wholly efficient when faced with the real industrial environment. At this stage, the experimental data show only that the concept does work and that more detailed investigation is required to improve metal removal efficiency.

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APPENDICES

APPENDIX A REFINERY WASTEWATER CHARACTERISATION

MATERIALS AND METHODS

The wastewater was characterised in order to determine the physical, biological and chemical characteristics, and the concentration of these components in the wastewater. These data guide the choice of method used for reducing possible pollutant concentrations. A detailed understanding of the nature of the wastewater to be treated is also essential when designing and operating collection, treatment and disposal facilities (Tchobanoglous and Burton, 1991).

Acidity and solids content (total, suspended and dissolved) were measured according to Standard Methods (APHA *et al*., 1998). Further measurements were made using colorimetric methods based on the principles of Standard Methods (APHA *et al*., 1998): ammonia (Spectroquant kit 1.14752, analogous to method 4500-NH3 G), chloride (Spectroquant kit 1.14897, analogous to method 4500 Cl- E), COD (Spectroquant reagents 1.14679 and 1.14680, analogous to method 5220 D), nitrate (Spectroquant kit 1.14773), nitrite (Spectroquant kit 1.14776), phosphate (Spectroquant kit 1.14842, analogous to method 4500-P C), sulphate (Spectroquant kit 1.14791) and sulphide (Spectroquant kit 1.14779). All kits were obtained from Merck Chemicals (Pty) Ltd South Africa, and used according to their instructions. Results were obtained by using a Spectroquant Nova 60 photometer (South Africa). pH was measured using a Cyberscan 2500 meter (Eutech Instruments, Singapore). All metal concentration determinations were made using atomic absorption spectrophotometry (GBC 909 AA, Avanta, Australia). All metal standard solutions were prepared from 1000 mg/L stock solutions (Fluka, Switzerland) diluted with deionised water to the relevant concentrations. For all analyses the reagents were of laboratory grade. All glassware was acid washed in 5 % HNO_3 and rinsed in distilled water before use.

RESULTS AND DISCUSSION

The wastewater analysis was compared to guidelines set out by the Department of Water Affairs and Forestry (DWAF) (1996) for water of quality suitable for reuse in an industrial environment. Category 4 reuse guidelines were chosen for the comparison, these are the least stringent as the water is used for activities such as ash quenching, transport, dust suppression, fire fighting, irrigation and rough washing (DWAF, 1996). The results in Table 2.4 indicate that the wastewater contains high levels of acidity (3.67 $gCaCO_3/L$), high ammonia levels (14.18 g/L), excessively high chloride content (44.17 g/L), high concentrations of sulphate (5.67 g/L) and COD (26.68 g/L) and has a very low pH (1.2 – 1.5). The other ions measured were not found to be in excessively high concentration, e.g. only approximately 20 mg/L phosphate and less than 1 mg/L nitrite. The solids analysis of the wastewater, showed a somewhat high total solids concentration of > 400 mg/L, 75 % of which was present in dissolved form (± 350 mg/L). The suspended solids fraction was also high when compared to the DWAF guidelines.

Table A.1 Wastewater non-metallic characteristics.

Character	Wastewater	DWAF guidelines for industrial disposal
Acidity ($gCaCO_3/L$)	3.67 ± 0.12	n/a
Ammonia (g/L)	14.18 ± 0.21	n/a
Chloride (g/L)	44.17 ± 7.57	0 – 0.5
COD (g/L)	26.68 ± 5.27	0 – 0.075
Nitrate (mg/L)	660.00 ± 42.43	n/a
Nitrite (mg/L)	0.23 ± 0.06	n/a
pH	1.2 – 1.5	5 – 10
Phosphate (mg/L)	21.67 ± 0.29	n/a
Sulphate (g/L)	5.67 ± 0.42	0 – 0.5
Sulphide (mg/L)	0.57 ± 0.29	n/a
Total solids (mg/L)	436.1 ± 38.2	0 – 1600
Total dissolved solids (mg/L)	347.6 ± 21.7	n/a
Suspended solids (mg/L)	44.9 ± 11.5	0 – 25

Table 2.5 shows the concentrations at which a number of metals are present in the wastewater. As expected, the PGM content is low due to the high recovery efficiency of the refining process. A small base metal content is present, and in all cases, this does not greatly overstep the limits set by DWAF. There is a very high level of sodium (1.82 g/L), which, when combined with the extremely high chloride content results in a very high ionic strength wastewater.

Compared to the Department of Water Affairs and Forestry guidelines listed alongside the characteristics in the tables, the wastewater is, in many cases, not suitable for reuse in industrial processes. Table 2.6 indicates (according to DWAF), the constituents of wastewaters that may cause problems if the water is reused without pretreatment. It is evident from the table that this wastewater requires treatment before reuse in order to minimise problems such as those listed in the table. The areas in which iron and manganese are implicated may not prove problematic, as the concentration of these constituents in the wastewater is at or below the levels set by DWAF. Conversely, the levels of pH, chloride, COD, sulphate and suspended solids would all lead to problems such as corrosion, fouling and blockages in the process.

Table A.2 Metal characteristics of the wastewater.

Metal (mg/L)	Wastewater	DWAF guidelines for industrial disposal
Rhodium	65 – 70	n/a
Gold	< 1	n/a
Palladium	< 0.1	n/a
Platinum	< 0.01	n/a
Cobalt	1.31 ± 0.01	n/a
Copper	25.56 ± 0.29	n/a
Iron	10.43 ± 0.05	0.0 – 10.0
Magnesium	3.92 ± 0.12	n/a
Manganese	0.27 ± 0.003	0.0 – 10.0
Nickel	13.80 ± 0.12	n/a
Sodium (g/L)	1.82 ± 0.009	n/a

The concentration of other ions measured in the wastewater was not sufficiently high to be considered harmful if the water were to be reused in any of the activities listed. In light of continued population growth, ongoing contamination of both ground and surface waters, uneven distribution of water resources and periodic droughts, consideration must be given to remediating this water, as its reuse within the refinery would symbolise a considerable saving in terms of water required from surrounding municipalities already struggling to provide enough water for domestic uses. The overall makeup of the wastewater does characterize it as a harsh and probably toxic environment for bioremediation via living organisms, but processes where the bioremediating agent is separated from the wastewater, such as the EMBR process, may be successful in rendering this water useful in some way.

Table A.3 Constituents of wastewaters that may contribute to reuse problems (DWAF, 1996).

Problem	**pH**	**Fe**	**Mn**	**SO_4**	**Cl**	**SS**	**COD**
Corrosion	■	■		■	■	■	■
Scaling	■	■		■		■	
Fouling		■	■			■	■
Blockages	■	■	■	■		■	■
Abrasion				■		■	
Embrittlement	■				■		
Discolouration	■	■	■				■
Resin blinding	■	■	■	■		■	
Foaming	■						■
Sediment	■	■	■	■		■	
Gas production	■			■			■
Taste/odours	■	■	■		■		
Precipitates	■	■	■	■			
Turbidity	■	■		■		■	■
Colour	■	■	■				■
Biological growth	■	■	■	■		■	■

In terms of recovering the rhodium from the wastewater, a biological method involving the immersion of a live recovering agent in the wastewater will not result in a sustainable process. Processes where the rhodium may be recovered biologically without adverse conditions harming the agent may find an application in this particular case, such as biosorption or the EMBR process. Physico-chemical methods may also be applicable if they can be engineered to tolerate the possible problems inherent in treating this wastewater, e.g. corrosion and scaling. A further problem that may hamper the recovery of the rhodium from this wastewater is the presence of nitrate ions, which may bind strongly to the rhodium-chloride complexes, making the metal almost completely unextractable. Recovery of the rhodium present in the wastewater represents a considerable increase in rhodium metal values. A simple approximate calculation using the average rhodium price for October 2004 shows that for every 500 L processed with 100 % efficiency, a gross profit of $1235 is made.

APPENDIX B CONTROL DATA FROM ISOTHERM EXPERIMENTS

MATERIALS AND METHODS

Control flasks were prepared as described in materials and methods section 5.6.1. No yeast biosorbent was added; pH adjustments were made as necessary.

RESULTS

In order to determine whether spontaneous precipitation of rhodium ions took place within the flasks during the isotherm experiments, control flasks (without biomass) were treated in exactly the same was as the experimental flasks. The comparison shown in figure B.1 illustrates that at all three pH values tested, the rhodium concentrations remained approximately equal at each equilibrium time. What the graph also shows is that at pH 1, the rhodium ions seem slightly less soluble, i.e. a lower concentration exists within the pH 1 flasks at every addition number.

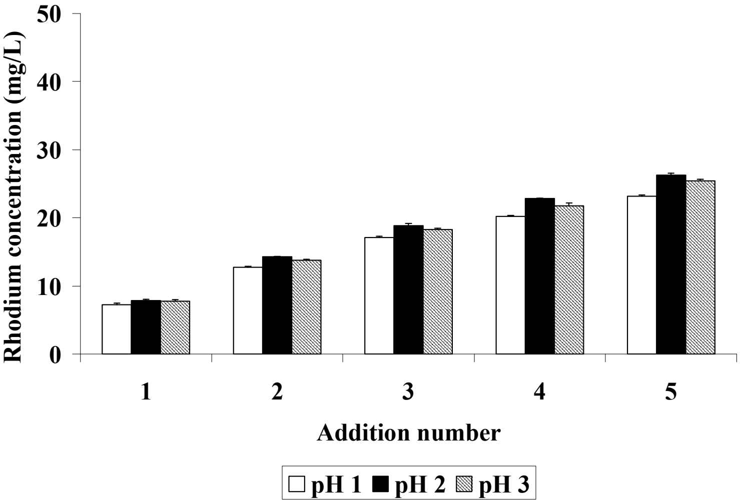

Figure B.1 Bar graph comparison of the metal concentrations in solution in the control flasks during the iosotherm experiments.