

**REMOVAL AND RECOVERY OF COPPER FROM
ELECTROPLATING RINSE WATER VIA A
GALVANIC CEMENTATION SYSTEM**

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UNIVERSITI SAINS MALAYSIA

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ELECTROPLATING RINSE WATER VIA A
GALVANIC CEMENTATION SYSTEM**

by

HOR YEAN PHIN

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NOMENCLATURE

a	intercept of a regression line
A_e	specific surface area, m^{-1}
C_{inlet}	inlet copper (II) concentration, $mol L^{-1}$
C_{outlet}	outlet copper (II) concentration, $mol L^{-1}$
C_0	copper (II) concentration at treatment time = 0, $mol L^{-1}$
C_t	copper (II) concentration at treatment time t , $mol L^{-1}$
D	diffusion coefficient, $m^2 s^{-1}$
E°	standard potential, V
F	Faraday constant, $96\ 485\ A\ s\ mol^{-1}$
I_L	limiting current, mA
k_m	mass transfer coefficient, $m\ s^{-1}$
M	molecular weight, $g\ mol^{-1}$
n	charge of the electrodeposited metal ion
Q	volumetric flow rate, $L\ s^{-1}$
Re	Reynolds number, $uv^{-1}A_e^{-1}$
s_B	standard deviation of blank
$s_{y/x}$	standard deviation of y-residuals in a standard calibration curve
Sc	Schmidt number, νD^{-1}
Sh	Sherwood number, $k_m \varepsilon A_e^{-1} D^{-1}$
V_e	cathode volume, cm^3
V_T	total volume of catholyte (cell + reservoir), cm^3
V_R	cell volume, cm^3
y_{dl}	detection limit

y_B	signal from blank
ε	porosity
u	flow velocity, m s^{-1}
ν	kinematic viscosity, $\text{m}^2 \text{s}^{-1}$
v_D	volumetric flow rate, $\text{cm}^3 \text{h}^{-1}$
μ	viscosity, $\text{g m}^{-1} \text{s}^{-1}$
ρ_w	water density, $1.00 \times 10^{-6} \text{g m}^{-3}$
ρ	space-time yield, $\text{g L}^{-1} \text{h}^{-1}$
ρ_s	space-velocity, $\text{L L}^{-1} \text{h}^{-1}$

PENGGUNAAN SISTEM PENYIMENAN GALVANI DALAM PENYINGKIRAN DAN PEROLEHAN SEMULA KUPRUM DALAM AIR BUANGAN INDUSTRI PENGELEKTROSADURAN

ABSTRAK

Suatu sistem galvani yang menggunakan sel alir telah diperkenalkan dalam penyingkiran kuprum dalam air buangan. Penyelidikan ini menilai keupayaan proses penyimenan galvani dalam menyingkirkan kuprum dari air buangan industri pengelektrosaduran di samping memperoleh semula logam kuprum. Proses ini tidak memerlukan bekalan tenaga luar kerana pertukaran kimia antara gandingan kuprum/ferum berlaku secara spontan. Oleh yang demikian, sistem ini amat menarik dalam pengurangan kos operasi, lebih-lebih lagi dalam rawatan air buangan cair. Ia juga merupakan salah satu alternatif bagi teknik rawatan yang sedia ada. Dua jenis mod operasi, iaitu laluan tunggal and laluan berganda, telah dikaji. Bahagian pertama kajian merangkumi penilaian prestasi sistem laluan tunggal berdasarkan keupayaan katod, kadar alir katolit, kepekatan awal kuprum (II) dan jenis katod yang digunakan. Keputusan menunjukkan sistem sel alir ini mampu menurunkan kuprum dalam air buangan tiruan ke bawah had maksimum yang dibenarkan. Namun demikian, kepekatan kuprum di bawah 1.0 mg L^{-1} tidak dapat dikecapi dalam sebarang keadaan dalam rawatan air buangan industri pengelektrosaduran. Dengan ini, satu mod operasi bagi reaktor elektrokimia yang lain perlu dikaji untuk meningkatkan keupayaan penyingkiran kuprum.

Bahagian kajian yang kedua melibatkan penggunaan reaktor galvani laluan berganda yang beroperasi pada kadar alir antara 3.8 mL min^{-1} dan 500 mL min^{-1} .

Elektrod tiga dimensi iaitu 80 ppi karbon kaca berongga (reticulated vitreous carbon) telah digunakan. Kajian pemindahan jisim telah menunjukkan koefisien pemindahan jisim purata berkadar dengan nombor Reynolds, Re^f , di mana $f = 0.68$. Perbandingan antara prestasi reaktor laluan tunggal and laluan berganda telah dijalankan dengan menggunakan kepekatan awal kuprum 10 mg L^{-1} , 100 mg L^{-1} dan 500 mg L^{-1} . Sebanyak 500 mL air buangan industri pengelektrosaduran yang mempunyai kepekatan kuprum awal 74.2 mg L^{-1} dan nilai konduktiviti 1.2 mS cm^{-1} telah dirawat dengan reaktor laluan berganda ini. Didapati reaktor yang beroperasi pada kadar alir 500 mL min^{-1} dapat menurunkan kuprum ke bawah 1.0 mg L^{-1} dalam masa 150 minit.

Penyelidikan tambahan ke atas jenis larutan kuprum lain menunjukkan keputusan yang amat memuaskan terutama sekali dengan larutan kuprum (II) fluoborat dan kuprum (II) sulfat. Kapasiti maksimum reaktor juga telah ditentukan. Corak penyimenan kuprum di atas karbon kaca berongga telah diperhatikan dengan mikroskop optik. Selain itu, ciri-ciri mikroskopik kuprum pula dikaji dengan menggunakan mikroskop elektron pengimbas (SEM) dan analisis spektrometri penyerakan tenaga X-ray (EDAX) telah dilaksanakan untuk memastikan kehadiran kuprum pada katod.

ABSTRACT

A galvanic system for the removal of copper from aqueous solutions using a divided flow-through cell is proposed. The present study looks into the feasibility of removing copper from dilute electroplating rinse water and recovering it in metallic form by a galvanic cementation process. This process does not require an external supply of energy due to the spontaneous chemical reaction between the copper/iron couple. Therefore, this operation is attractive in reducing operating costs, especially when dealing with low ion concentrations and serves as an alternative to current wastewater treatments available. Two types of operating modes (single-pass and batch-recycle) have been investigated. Initially, the performance of the proposed single-pass system was evaluated as a function of cathode potential, catholyte flow rates, initial copper (II) concentration and types of electrode materials used. Results have shown that the galvanic flow system can remove copper effectively below the maximum permissible level from simulated copper (II) solutions. However, an outlet copper concentration below 1.0 mg L^{-1} was not achieved with any condition when treating industrial wastewater. Therefore, another mode of operation of electrochemical reactor has been attempted to achieve higher efficiency of copper removal.

The second part of this work describes a batch-recycle galvanic reactor that operates at flow rates ranging from 3.8 mL min^{-1} to 500 mL min^{-1} . A three-dimensional cathode, 80 ppi reticulated vitreous carbon, was used for this purpose. Mass transfer studies show that the average mass transfer coefficient was proportional to the Reynolds number, Re^f , where $f = 0.68$. A comparison of the performance between a single-pass and a batch-recycle reactor was also conducted with an initial copper concentration of 10 mg L^{-1} , 100 mg L^{-1} and 500 mg L^{-1} . A 500 mL feed of 74.2 mg L^{-1} of copper in

electroplating rinse water with a low conductivity of 1.2 mS cm^{-1} was reduced to less than 1.0 mg L^{-1} in 150 minutes with a batch-recycle reactor operating at a flow rate of 500 mL min^{-1} .

Additional work on the treatment of other copper plating baths showed satisfactory results especially with copper (II) fluoborate and copper (II) sulphate solutions. The capacity of the batch-recycle galvanic reactor was also determined. Parametric studies of the copper deposition on reticulated vitreous carbon were made using the optical microscope. A Scanning Electron Microscopy (SEM) investigation was performed to study the microscopic features of the copper deposits and X-ray energy dispersive spectrometry (EDAX) analysis was executed to confirm the presence of copper recovered on the electrode.

CHAPTER 1 INTRODUCTION

Copper is a metal of great importance in industrial use. The large consumption of copper in industry is due to its properties of electric conductivity, ductility and thermal conductivity. It is used extensively in the production of pipes, alloys, fertilizers, wire, brass, cooking utensils, motor vehicles and air-craft plating (Forstner & Wittmann, 1983). Although copper is known to be a biologically essential element to all living things, the presence of excessive copper in the environment poses potential toxic effects on aquatic life as well as to animal, plant life and humans (Watson, 1973; Scheinberg, *et al.*, 1977; Copper Connects Life, 2001a, b & c). Primary sources of copper in industrial waste streams are metal finishing operations, which include electroplating, electroless plating and printed wire board (PWB) manufacturing.

1.1 Metal Finishing Operations

Metal finishing is the process of changing the surface of a workpiece, for the purpose of improving its appearance and/or durability. Most metal finishing operations involve three basic steps: pretreatment, which involves the use of solvents, alkaline cleaners, abrasive materials and water; plating, which involves changing the surface by putting a new a metal layer; and post-treatment to remove chemical residues or byproducts of plating and to assist in drying. In between these steps, a rinsing cycle is essential to remove the thin film of concentrated chemicals (drag-out) that adheres to parts after their removal from the process bath (plating solution). Ineffective rinsing will result in rejection of the product. In order to achieve high quality rinsing, the concentration of contaminants in the rinse bath should be kept within a specific tolerable level that differs from process to

process. Electroplating operations are performed in baths, then followed by a rinsing cycle or a series of rinsing cycles as shown in Figure 1.1.

1.1.1 *Copper Plating*

Copper plating is widely used as an underplate for nickel and chromium decorative coatings as well as in electroforming and the production of PWB. The general types of electrolytes for copper bath are acid-(sulphate and fluoborate); alkaline-(cyanide); and mildly alkaline-(pyrophosphate) complexed baths (Bair & Graham, 1974; Dini, 1974; Safranek, 1974; Snyder, 2002a, b & c).

1.1.1(a) *Acid-(sulphate and fluoborate) electrolyte*

The copper sulphate bath is the more frequently used of the acid copper electrolytes. Besides having higher throwing power compared to copper fluoborate, it is more economical to prepare, operate and treat. But, the fluoborate ions from fluoboric acid provide enhanced solubility and conductivity as well as high plating speeds. The acid copper bath is used primarily in electroforming and decorative plating operations.

1.1.1(b) *Alkaline-(cyanide) electrolyte*

In contrast to acid copper baths, alkaline-(cyanide) copper baths have better throwing power and thus exhibit greater advantage in plating a more complicated shaped workpiece. The drawback of this bath solution is that the highly poisonous cyanide needs to be treated with complete destruction. Recently, works on non-cyanide processes have been studied intensively (Cleaner Production Guidebook, 2002a & b).

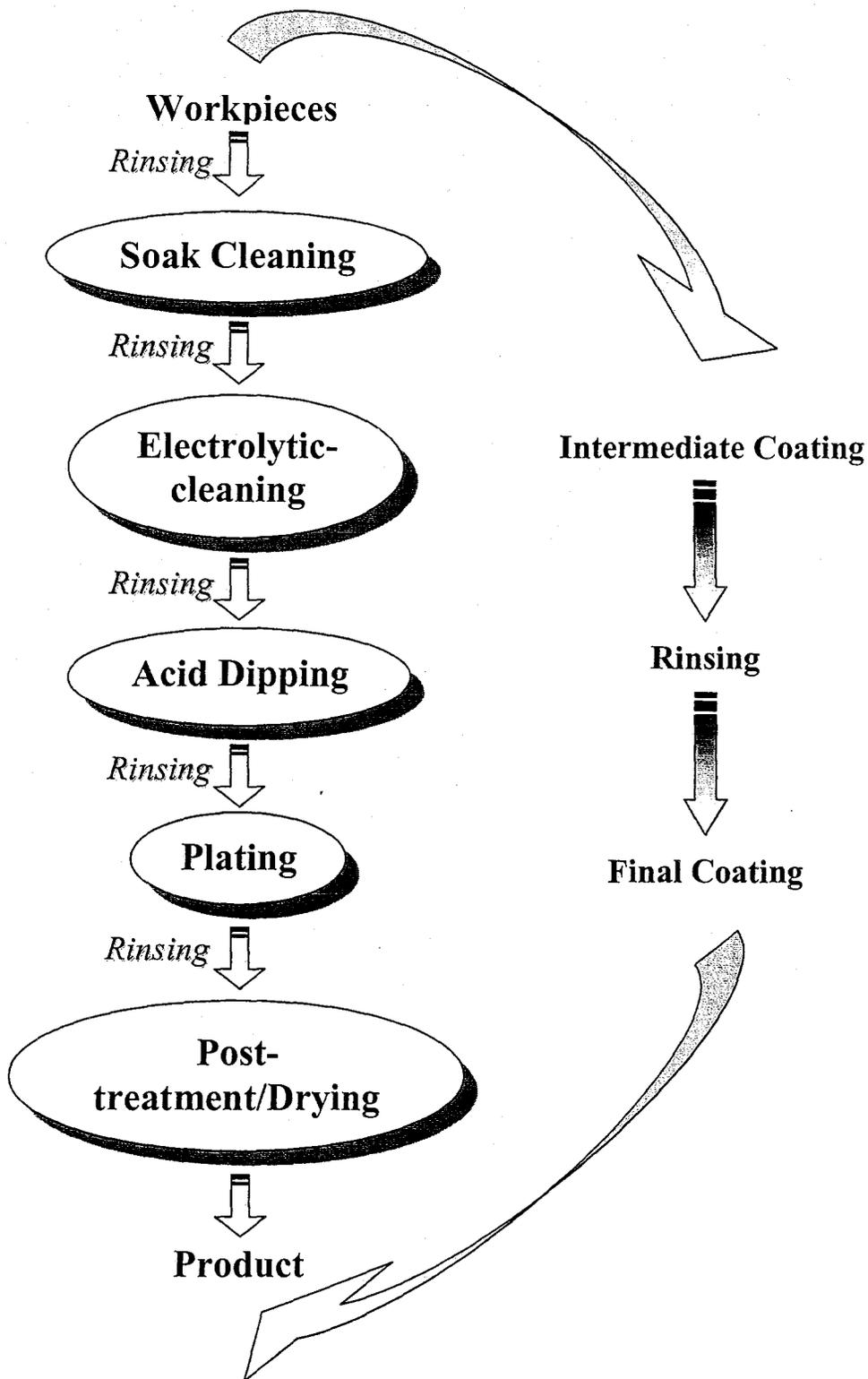


Figure 1.1: A typical process flow chart for a general electroplating operation (Hong Kong Cleaner Production Centre, 2002).

1.1.1(c) *Alkaline-(pyrophosphate) electrolyte*

It exhibits good throwing power and produces coating with good ductility. The bath is used primarily to produce thick deposits especially in the fabrication of through-hole PWB. However, its waste effluent is more difficult to treat.

1.1.2 *Metal Finishing Waste Streams*

Metal finishers differ widely in the types of items they plate and finishing processes that are required. However, some waste streams that are commonly found are solvents used for cleaning the parts, the solutions from plating baths which contained metals, cyanide or acid solutions and the rinse water. Some of the toxic waste products released are heavy metals such as copper, chromium, nickel, zinc and others. One of the major problems in the metal finishing operations and maintenance of plating lines is the rinse water (Cleaner Production Guidebook, 2002c). A rinse tank can be likened to a dilute plating tank. It has the same chemicals as in the plating tank, in the same proportion, but at a lower concentration. Large volumes of wastewater are generated during rinsing operations. Copper concentrations in the rinse water may range from a value as low as 0 mg L⁻¹ to 131 mg L⁻¹ (Watson, 1973; Lin, *et al.*; 1999; Inman, *et al.*, 2002).

1.2 **Environmental Regulations**

In the United States, wastewater discharges from electroplating and other metal finishing operations are currently regulated by the Environmental Protection Agency (EPA) federal standards 40 CFR 413 and 433 (Electronic Code of Federal Regulations, 2002a & b). The maximum level per day for copper under the pretreatment standards is 4.5 mg L⁻¹ for existing sources of electroplaters and 3.38 mg L⁻¹ for new sources of metal finishers.

USEPA also requires 1.3 mg L^{-1} in drinking water as the current enforceable copper concentration action level (Skipton & Hay, 1998).

The report by United States-Asia Environmental Partnership (2002) stated that chemical and electronics industries in Malaysia account for 12 percent of the country's major industrial polluters. In 1994, the Ministry of International Trade and Industry (MITI) reported that more than 417, 400 metric tons of toxic and hazardous wastes were generated by industries and this amount will continue to increase. The 1979 Environmental Quality (Sewage and Industrial Effluents) Regulations sets 0.2 mg L^{-1} and 1.0 mg L^{-1} as the copper discharge limit in catchment areas located upstream of domestic water supply and inland water respectively (Lembaga Penyelidikan Undang-undang, 1997). The local small to medium (SMI) electronics and electroplating industries were found to dispose effluents containing heavy metal contaminants in domestic sewage drains without prior treatment (United States-Asia Environmental Partnership, 2002). Due to the shortage of toxic waste storage facilities, there is a tendency in the metal finishing industries to redesign their processes from open to closed systems. Metal finishers should make use of cost-effective wastewater treatment systems to recover and recycle heavy metals from wastewater effluent.

1.3 Treatment Technologies

Apart from the toxicity of copper, the value of copper metal frequently makes recovery processes important. Therefore, treatment of copper-bearing wastewater usually involves removal and recovery processes. An overview of the commonly used treatment technologies is summarized in Table 1.1. These include precipitation, ion exchange, solvent

Table 1.1: Current treatment technologies for the removal and recovery of copper.

	Treatment technologies	Details	Some examples of references
1.	Precipitation	This is the most widely used method for removing copper because of its simplicity. The reagents used to precipitate copper as insoluble hydroxide of alkaline pH or as sulfides include lime, caustic soda, oxalic acid, hydrogen sulphite and soluble sulphides. It is no longer applicable due to health hazards associated with the disposal of large quantities of precipitated sludge, high cost of sludge disposal in landfills and secondary pollution.	Watson (1973), Pickett (1979), Galitskii, <i>et al.</i> (1993), Baltpurvins, <i>et al.</i> (1997), Gyliene, <i>et al.</i> (1997).
2.	Ion Exchange	It involves removal, recovery and preconcentration of copper as well as purification of rinse water for reuse purposes. It is also efficient in removing copper ions from dilute solutions and handling dilute feed. Moreover, it does not present a sludge problem and has the advantage of reclamation of copper. Besides the high capital costs involved in using ion exchange resins, strong acid and alkaline solutions are needed to regenerate the resins and the resulting solutions can be directly returned to the plating tank or must under go reclamation or further treatment.	Patterson (1975), Chew & Nelson (1997), Grubisa, <i>et al.</i> (1994), Dobrevsky, <i>et al.</i> (1997), Renz, <i>et al.</i> (1998).
3.	Solvent/Membrane Extraction	It uses mainly chelating compounds as organic solvents for extraction. It is inefficient in treating low metal ion concentrations, as more extraction stages are required. Organic solvent and acid losses often occur. Recently, some authors (Luo & Zhang, 1998 and Valenzuela, <i>et al.</i> , 1999) have gone a step further in the development of membrane-based solvent extraction. It shows improved efficiency when combined with ion exchange, electrowinning or membrane process.	Pickett (1979), Nyman, <i>et al.</i> (1995), Dreisinger, <i>et al.</i> (1996), Luo & Zhang (1998), Renz, <i>et al.</i> (1998), Valenzuela, <i>et al.</i> (1999).

Table 1.1, continued:

	Treatment technologies	Details	Some examples of references
4.	Evaporation	Natural or heat evaporation is commonly used. Heat evaporation is divided into atmospheric and vacuum evaporations. Atmospheric evaporators are inexpensive compared to vacuum evaporators and the later recycles rinse water. One problem with this technology is impurity buildup that needs further treatment.	Watson (1973), Jabrani, <i>et al.</i> (1996), Dillon (1999), Stephen R. Schulte (2002).
5.	Membrane Processes	The most commonly used are reverse osmosis (RO) and electrodialysis. In RO units, diluted or concentrated rinse waters are forced through a semi-permeable membrane at pressures greater than aqueous osmotic pressure resulting in the separation of water from the plating chemical such as copper ions. Electrodialysis recovers and concentrates dilute solutions or rinse waters. The direct electrical current applied selectively drive metal ions through a series of alternatively placed cationic- and anionic-permeable membranes, producing concentrated and purified streams. Its efficiency drops as the purity of treated solutions increases due to the lower electrical conductivities. This treatment technology suffers from membrane durability problems and thus involves high operating cost.	Pickett (1979), Bobrinskaya, <i>et al.</i> (1995), Ogutveren, <i>et al.</i> (1997), Dillon (1999), Stephen R. Schulte (2002), Wong, F.-S., <i>et al.</i> (2002).
6.	Adsorption	It has a lot of potential for copper removal using activated carbon but it is costly. As an alternative, it could be more economical to use low-cost adsorbents like apple wastes, rocks minerals, chitosan, soil, oil shale and wood powder.	Panday, <i>et al.</i> (1985), Inoue, <i>et al.</i> (1992), Khalfoui, <i>et al.</i> (1995), Singh, <i>et al.</i> (1996), Lee & Yang (1997), Sulochana, <i>et al.</i> (1998), Ajmal, <i>et al.</i> (2001), Al-Asheh & Banat (2001).

Table 1.1, continued:

	Treatment technologies	Details	Some examples of references
7.	Chemical Reduction	<p>Chemical reductants like hydrogen gases, sulphur dioxide gases, sodium borohydride and sodium hypophosphite are employed in the removal of copper. Another process of chemical reduction is direct cementation of copper (metal displacement) on reducing agents such as scrap iron in the form of chips or powder and aluminium powder. Unfortunately, the resulting product (combined copper-reductant) is physically inseparable.</p>	<p>Watson (1973), Stern (1976), Pickett (1979), Gomez-Lahoz, <i>et al.</i> (1992), Comsa, <i>et al.</i> (1993), Ku, <i>et al.</i> (1994), Bolser (1995), Serna, <i>et al.</i> (1996), Nagashima (1997), Stefanowicz, <i>et al.</i> (1997), Tushurashvili, <i>et al.</i> (1997).</p>
8.	Electrochemical Processes	<p>This technology covers both electrolytic and galvanic processes where copper can be removed prior to discharge via a redox reaction. A major advantage of this technology is that the metal can be recovered and recycled in one step to decrease the amount of copper lost in the drains, and yet no chemicals are used. However, electrolytic processes are less cost-effective when dealing with very low metal ion concentrations.</p>	<p>Genders & Weinberg (1992), Walsh & Mills (1993), Rajeshwar, <i>et al.</i> (1994).</p>

or membrane extraction, evaporation, membrane processes, adsorption, chemical reduction and electrochemical processes. Due to the high cost of these methods, there is a need for the development of a method that is not only cost-effective, but can be easily operated. A report describing the application of galvanic coagulation technology for wastewater treatment (Wastewater Technology, 2000) was found to perform more efficiently at a lower cost than current available treatment technologies. Utilizing a rotated drum filled with coke and scrap iron and/or aluminum reactor, a filter, fluid pumps and a control panel, contaminants were removed by chemical or electrochemical reactions, co-precipitation and adsorption.

1.4 Electrochemical Technology

As environmental legislation become more stringent, requirements for cleaner wastewater treatment technologies have become necessary. The electrochemical methods prove to have the ability to recover metals in pure and saleable metallic form without any addition of chemicals (Zee & Newman, 1977; Tison, 1981; Widner, *et al.*, 1998). Besides being a clean and versatile approach, recovering and recycling both the metal and the water provide great economic benefits.

Table 1.2 illustrates some of the progress in the development of electrochemical methods for effluent treatment. Electrochemical reactors may either operate in static batch or continuous flow mode. In electrochemical methods, the reactors can be classified as electrolytic or galvanic systems. The reactors are based on either a two- or three-dimensional electrode. Since the two-dimensional electrode has low specific surface area for effluent treatment, it is less favorable unless more concentrated solutions are involved. Campbell and his co-workers (1994) had proven

Table 1.2, continued:

Operation mode and electrode geometries	System type	Metal ions of interest [concentration range]	Remarks	References
ii. Titanium or stainless steel plate (cathode) and titanium net (anode)	Electrolytic (Single-pass)	Cu (II) [340 mg L ⁻¹]	The influence of the flow rate on removal efficiency and current yield was studied. Though the reactor needs only low capital cost, the two-dimensional cathodes could not reduce copper concentration below 5 mg L ⁻¹ in any condition.	Solisio, <i>et al.</i> (1999)
<i>b) Three-dimensional cathode</i>				
i. Carbon particles (cathode) and mixture of carbon and copper powder (anode)	Electrolytic (Single-pass)	Ag (I) [1000 mg L ⁻¹]	The concentration of silver was successfully reduced to less than 1 mg L ⁻¹ in a 5.5 cm thick bed and to less than 10 mg L ⁻¹ in a 4.0 cm thick bed.	Zee & Newman (1977)
ii. Copper-plated steel spheres (cathode) and lead wire (anode)	Electrolytic (Single-pass and batch-recycle)	Cu (II) [10-500 mg L ⁻¹]	A tumbled-bed electrochemical reactor works well for the recovery of copper from dilute acid copper systems. The performance of the reactor at various initial copper concentrations was compared based on the operating costs and capital costs.	Tison (1981)
iii. Stainless steel grids (cathode and anode)	Electrolytic (Batch-recycle)	Ag (I) [120-983 mg L ⁻¹]	A silver recovery cell operated under galvanostatic and potentiostatic conditions is described. Treated solution of about 1 mg L ⁻¹ was achieved with satisfactory mean current yields.	Enriquez-Granados, <i>et al.</i> (1983)

Table 1.2, continued:

Operation mode and electrode geometries	System type	Metal ions of interest [concentration range]	Remarks	References
iv. Stainless steel (cathode) and graphite (anode)	Electrolytic (Single-pass)	Cu (II) [1-5 g L ⁻¹]	The concentration of copper was reduced to 0.1 g L ⁻¹ after treatment. The reduced copper at the cathode is in the form of small and loose particles, which do not adhere to the cathode itself. However, they are large enough to settle in the system by hydraulic sluicing.	Samhaber (1988)
v. Graphite felt (cathode)	Electrolytic (Batch-recycle)	Ag (I) [14-540 mg L ⁻¹]	Silver recovery was carried out at cathode potentials of -550 and -650 mV vs SCE. Below 50 mg L ⁻¹ of copper, further decrease in potential is needed to yield good faradaic efficiency.	Tricoli, <i>et al.</i> (1993)
vi. Reticulated vitreous carbon (cathode) and stainless steel plate (anode)	Electrolytic (Batch-recycle)	Pb (II) [8.2-137.2 mg L ⁻¹]	The concentration of lead ion was reduced to 0.1 mg L ⁻¹ with recirculation times ranging from 20 minutes to 2 hours, depending on the reticulated vitreous carbon porosity and the flow rate. A system operating at 240 L h ⁻¹ with a cathode porosity of 80 ppi yields the best removal rate.	Widner, <i>et al.</i> (1998)

Table 1.2, continued:

Operation mode and electrode geometries	System type	Metal ions of interest [concentration range]	Remarks	References
vii. Packed bed (cathode) and gas diffusion (anode)	Galvanic (Batch-recycle)	Fe(III) [20 mol m^{-3}]	This reactor works based on the catalytic oxidation of hydrogen gas in the anode and the simultaneous reduction of metal ions on the cathode. The reduction of ferric ions in a GBC-reactor is controlled by mass transfer and electrochemical kinetics.	Zwart, & Janssen (1998)
viii. Copper foam (cathode) and titanium net (anode)	Electrolytic (Batch-recycle)	Cu (II) [340 mg L^{-1}]	The best performance of a reactor with 98 % recovery was obtained at a high flow rate of 1000 L h^{-1} .	Panizza, <i>et al.</i> (1999)
ix. Graphite felt or stainless steel wool (cathode) and stainless steel (anode)	Electrolytic (Single-pass)	Cu (II) [150 mg L^{-1}], Zn (II) [200 mg L^{-1}]	A reactor using graphite felt and stainless steel wool managed to reduce copper concentration to less than 0.05 mg L^{-1} and 22.1 mg L^{-1} respectively. It was shown that a careful control of pH is necessary to minimize hydrogen evolution during zinc removal.	Paidar, <i>et al.</i> (2000)

that utilization of the three-dimensional packed bed electrode in the removal of nickel and copper is more efficient than a two-dimensional plate electrode experimentally. For dilute metal-bearing wastewaters, porous three-dimensional electrodes in the form of carbon (Bennion & Newman, 1972); metallic felt or foams (Marracino, *et al.*, 1987; Langlois & Coeuret, 1989); reticulated vitreous carbon (RVC) (Wang & Dewald, 1983; Ponce De Leon & Pletcher, 1996; Bertazzoli, *et al.*, 1997); carbon felt (Kinoshita & Leach, 1982; Carta, *et al.*, 1991) and stainless steel wool (Paidar, *et al.*, 2000) are often considered to provide high specific surface area and high overall mass transfer rates.

A number of electrochemical systems using new cell technologies for the removal of heavy metals are commercially available such as Chemelec Cell, Eco-Cell, Porocell and others (Genders & Weinberg, 1992; Pletcher & Walsh, 1993; Dalrymple, *et al.*, 2002). All these cells are categorized as electrolytic cells. These electrolytic cells operated less effectively in electrolytes of low electrical conductivities. Dilute solutions with low metal ion concentrations give rise to kinetic and thermodynamic limitations (Scott & Paton, 1993), requiring a high electrical power input to produce high recoveries. Therefore, the treatment of dilute solutions like rinse water using conventional electrolytic cells would result in high operating costs causing the electrochemical technique to be less economical. The alternative solution to these problems would be a system, which recovers and recycles both the metal and the water without any need of an external supply of energy. The galvanic process (an electrogenerative mode process) therefore should be further explored to provide the alternative to conventional electrolytic systems.

1.5 Objective

The aim of this work is to develop a new technology for in-process removal and recovery of copper from electroplating rinse water. The proposed system should minimize waste discharge by avoiding precipitation processes which require precipitants. This coupled with no requirement for external energy in turn will reduce the operating costs in effluent treatment. Studies were carried out to investigate the feasibility of removing copper in metallic form from dilute simulated solutions and real effluent samples below 1.0 mg L^{-1} . In this work, two types of operation mode, the single-pass and batch-recycle were investigated and the results were compared. This study covers evaluation of the performance of the system as a function of cathode potential, catholyte flow rates, initial copper (II) concentration and types of electrode materials used. The mass transfer characteristics during the galvanic cementation process were also examined for both operation modes. Other studies were also performed to include the determination of the capacity of the system, characterization of the recovered copper and its possible application on various types of copper plating baths.

CHAPTER 2 REVIEW OF GALVANIC CEMENTATION SYSTEMS

2.1 The Galvanic Cementation Processes

Cementation or known as 'the oldest chemical reduction' according to Pickett (1979) is a usual method of metal recovery in hydrometallurgical processes. It is a metal displacement reaction where metal ions from an aqueous solution are being precipitated spontaneously by a relatively more electropositive metal. An example is the cementation of copper on iron that acts as a base metal in a Cu/Fe couple (Figure 2.1). Simultaneous dissolution of iron and deposition of copper occur during the cementation process.

A galvanic cell is an electrochemical cell that converts chemical energy into electrical energy. It is a cell in which chemical reactions occur spontaneously at the electrodes when they are connected through an external circuit, producing a direct electrical current. As a consequence, one reagent must be oxidized and another must be reduced.

Direct cementation of copper onto high surface area packed beds of iron particles was reported by Wragg and Bravo de Nahui (1992). They have reported on the influence of initial copper (II) concentrations, pH, particle size, degree of oxygenation, presence of chloride ions and temperature in both single-pass and batch recirculation systems. Recovery of copper by direct cementation on iron scrap was studied by Serna, *et al.* (1996). The authors investigated the effect of iron scrap amounts, acidity and temperature on copper recovery. The results of these experiments showed 99 % copper removal and the purity of cemented copper was 85 to 90 %. Stefanowicz, *et al.* (1997) also investigated copper recovery by the same process from sulphate-based electroplating waste solutions and spent nitric acid-based etching solutions.

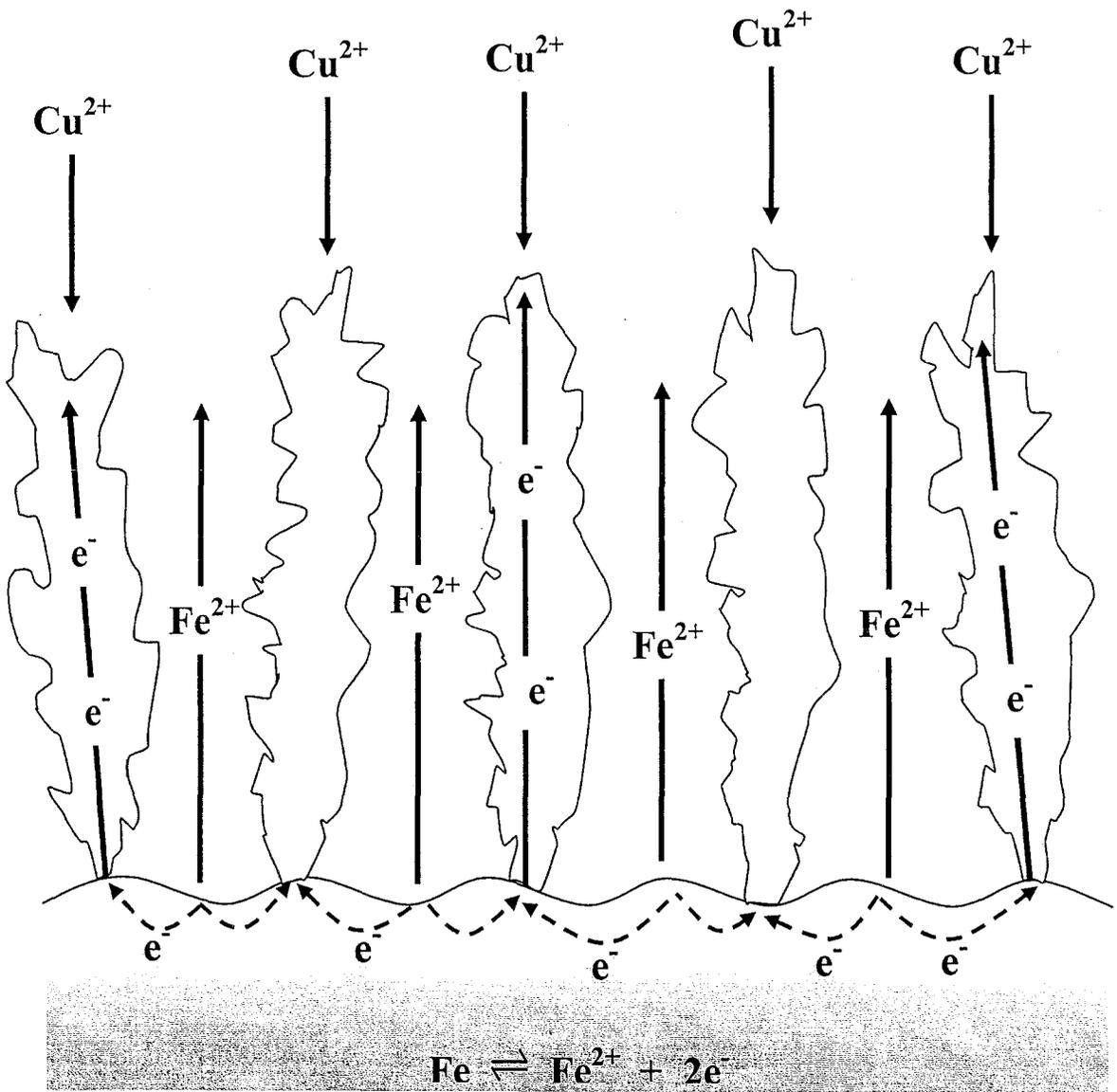
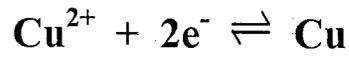


Figure 2.1: Direct cementation of copper on iron (Wragg & Bravo de Nahui, 1992).

However, direct cementation produces impure metal that needs further purification and the metal recovered is physically inseparable from the base metal. Another problem of this process is the excessive consumption of the more electropositive metal. Another limitation of the undivided cell design was the occurrence of 'chemical shorting' or poisoning of the reaction resulted by the free diffusion of reactants and products from one electrode to the other (Card, 1987).

Kumar and Vasu (1973) presented a novel approach by galvanic cementation for the recovery of copper from chalcopyrite leach liquors. In their approach, a cell was divided into two electrolyte compartments by a porous porcelain pot or chlorinated PVC diaphragm, with static copper (II) chloride-iron (II) chloride solution as catholyte and iron (II) chloride solution as anolyte. The authors reported that the use of a rotating copper foil cathode and a rotating mild steel anode resulted in the recovery of more than 99 % purity of copper with minimum iron consumption. A similar approach was also followed by Jain, *et al.* (1986). In their study, the purity of copper recovered by the galvanic cementation technique was more than 99.9 % compared to 87 % by direct cementation and 99.5 % by electrolytic techniques. The improvement in copper purity was due to the good selectivity, low resistivity, suitable porosity and reasonable resistance to chemical attack of the microporous rubber diaphragm used in their system.

Langer and Anderson (1976) patented a galvanic cementation process for the recovery of metals from aqueous solution. As described briefly in Table 1.2, the process used scrap iron as the sacrificial anode to precipitate copper metal from solutions of copper (II) in the Cu/Fe system. Examples of other systems include Cu/Ni, Cu/Zn and Cd/Zn systems where the more noble metals in the respective couples were recovered. The process was further evaluated for different anode and cathode metals, one fluid vs. two fluid

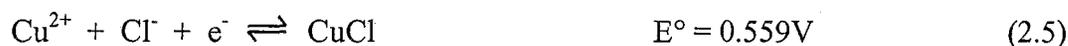
electrolytes, various anolytes and catholytes, exclusion of or access to air, effect of hydrogen gas evolution, effect of temperatures, etc. It was shown that this process was able to cement out metals from highly concentrated aqueous solutions. Prakash, *et al.* (1978) discussed the application of the galvanic cementation technique for winning pure copper from chalcopyrite leached with ferric chloride solution. Various factors which affect the deposition rate of copper such as anolyte acidity, catholyte composition, area of anode and cathode and cell resistance were studied.

The need to improve the galvanic cementation technique led to the development of a three-dimensional electrode cell operated under natural convection. Cell polarization as a result of varying initial copper sulphate concentrations from 0.05 M to 0.5 M and effects of bed height on the cell performance have been investigated by Sedahmed and Fawzy (1985). However, their galvanic static batch cell is not suitable for the treatment of dilute solutions like industrial wastewater. Recovery of precious metal like gold from cyanide leached solution using the galvanic cementation method was also performed by Darus, *et al.* (1993) and Zanariah (1996). Abdo and Sedahmed (1998) also used this method in the removal of hexavalent chromium from wastewater.

The galvanic system has been investigated over the past three decades. Surprisingly, the studies have received little attention. Despite its advantages, the stationary batch galvanic system which depends only on a slow process of free diffusion, exhibits limitation of mass transfer rate. Recent works have discussed the importance of forced convection to improve the efficiency of electrochemical methods for dilute wastewater treatment by providing intimate contact between the flowing stream and the electrode surface (Wang & Dewald, 1983; Conway, 1994; Yiu, 2000).

2.2 Galvanic Reduction of Copper

The possible main cathodic reactions in the electrochemical copper/iron couple system in the presence of chloride ions that have been considered are as follows (the values of E° were obtained from *Standard Potentials in Aqueous Solution*, 1985):



According to Mattsson and Bockris (1959), the electrochemical dissolution and deposition of copper in the acid sulphate system proceeds in two-step reactions (2.2) and (2.4) with the former one as a slower step. The observation of two one-electron reduction waves in the linear voltammograms of electrodeposition of copper onto vitreous carbon in the presence of chloride ions by Gunawardena, *et al.* (1985) has also proven this.

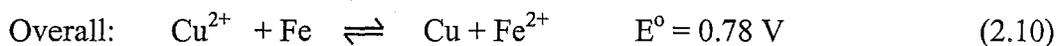
From equation (2.2) and (2.4), copper (I) readily disproportionates. However, without strong complexing agents like CN^- to stabilize copper (I), its concentration in pure aqueous solution is extremely low. This could be explained by the fact that the ratio of copper (I) concentration to copper (II) concentration is in the order of 10^{-6} (Well, 1984). Other competitive cathodic reactions (2.1), (2.6) and (2.7) include reduction of dissolved oxygen and hydrogen evolution. In the presence of chloride ions which might have migrated through the ion exchange membrane, reaction (2.5) tends to be another possible

competitive cathodic reaction. A comparison of the E° of the possible anodic reactions below when coupled with reaction (2.3), shows that oxidation of iron to iron (II) represents the more thermodynamically favoured reaction.



However, further oxidation of iron (II) to iron (III) by dissolved oxygen might take place as indicated by reaction (2.7) and (2.9).

Consequently, the major elementary steps in the galvanic reaction of copper/iron may be represented by the equations:



with the Gibbs free energy, $\Delta G^\circ = -150.5\text{kJ mol}^{-1}$. The fact that ΔG° is negative provides evidence of the spontaneous nature of the above overall reaction.

2.3 Operation Mode of Electrochemical Reactor

When evaluating an electrochemical reactor design in terms of its efficiency and operating costs, the choice of operation mode is often being considered as a decisive factor. In general, the three types of operation modes commonly adopted for wastewater treatment are static batch, single-pass and batch-recycle mode. Electrochemical reactors operating under natural convection, as in a static batch cell for example, was found to be inefficient when treating dilute wastewater (Sedahmed & Fawzy, 1985; Yiu, 2000). This inefficiency is due to the slow mass transfer process (i.e., the diffusion of a dissolved reactant from the

bulk solution to the electrode surface). Therefore, in order to improve the mass transfer process, either increased surface area of the electrode or minimized thickness of diffusion layer has to be employed. This could be achieved by adopting a mechanically assisted and enhanced hydrodynamic flow of the fluid to the high-area electrode or by movement of the electrode (Conway, 1994; Avci, 1998). Several papers have been published concerning the use of electrochemical reactors for the removal of heavy metals in a continuous single-pass mode and batch recirculation mode (Chu, *et al.*, 1974; Pletcher, *et al.*, 1991a & b; Pletcher, *et al.*, 1993). In a single-pass reactor, the electrolytes were passed through the cell once only. On the other hand, the electrolytes were continuously recirculated from the reservoirs to the cell and back to the reservoirs again in a batch-recycle reactor. The reservoirs were continuously stirred to provide homogeneous mixing. The batch-recycle system may be considered as a continuously stirred reactor (CSTR) if the V_T is much greater than V_e (Pletcher & Walsh, 1993). Unlike the single-pass reactor, both the inlet and outlet reactor concentrations are time-dependent.

2.4 Mass Transfer Studies

Mass transport in electrochemical flow cells may be described in the form of a power expression (Heitz & Kreysa, 1986):

$$Sh = mSc^b Re^f \quad (2.11)$$

The values for the constant m and the exponent b and f may be determined experimentally. The dimensionless Sherwood (ratio between effective mass transport and mass transport by molecular diffusion), Reynolds (ratio between inertia force and friction force) and Schmidt (ratio between momentum transport and mass transport by molecular diffusion) numbers in this correlation are defined as (Card, 1987):

$$Sh = \frac{k_m \varepsilon}{A_e D} \quad (2.12)$$

$$Re = \frac{u}{A_e \nu} \quad (2.13)$$

$$Sc = \frac{\nu}{D} \quad (2.14)$$

For flow systems, the Schmidt number usually appears to the power 1/3 (Carta, *et al.*, 1991). By substituting the experimental values of k_m obtained from the following sections into equation (2.12), the Sherwood numbers would be obtained. Subsequently, the Reynolds and Schmidt numbers would be calculated based on the experimental values for u and some physical properties of the electrolytes used in the system. With this, the linear regression analysis would be used to form equation (2.11).

2.4.1 *Single-pass Mode*

The single-pass reactor in this initial study was assumed as a plug flow reactor and this assumption will be verified later in this work. According to Heitz and Kreysa (1986) as well as Card (1987), the average mass transfer coefficient is defined in terms of concentration gradients by equation (2.15):

$$k_m = \frac{u}{A_e L} \ln \left(\frac{C_{\text{inlet}}}{C_{\text{outlet}}} \right) \quad (2.15)$$

with constant C_{inlet} and C_{outlet} that are independent of time at steady-state conditions.

2.4.2 *Batch-recycle Mode*

The batch-recycle reactor used in this study is considered as a CSTR and may be modeled as (Pletcher, *et al.*, 1991a; Ponce de Leon & Pletcher, 1995; Widner, *et al.*, 1998):

$$\ln (C_t/C_0) = -\frac{V_e k_m A_e}{V_T} t \quad (2.16)$$

From the slope of $\ln (C_t/C_0)$ against time linear plots, the values of k_m could be obtained.

2.5 Space-time Yield

The space-time yield, ρ is the amount of product which can be produced within 1 L of cell volume during 1 hour. It serves as an important figure of merit in describing the performance of an electrochemical reactor, especially as a basis for an objective comparison of performance. The amount of product refers to the amount of copper removed. In this case, the space-time yield is used to describe the comparison between a single-pass and a batch-recycle reactor. It can be calculated from space-velocity, ρ_s which is given by the following equations (Kreysa, 1981):

For a single-pass reactor:

$$\rho_s = \frac{v_D}{V_R} = \frac{\rho}{(C_{\text{inlet}} - C_{\text{outlet}})M} \quad (2.17)$$

For a batch-recycle reactor:

$$\rho_s = \frac{v_D}{V_R} = \frac{\rho}{(C_0 - C_t)M} \quad (2.18)$$

Rearrangement gives:

$$\rho = \frac{v_D (C_0 - C_t)M}{V_R} \quad (2.19)$$

where $V_R = V_e$ in this study since the electrode occupies a major part of the cell volume (Pletcher & Walsh, 1993).