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Extraction of Copper from Mining Residues by Rhamnolipids

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A Thesis

in

The Department

of

Building, Civil, and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
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Abstract

Extraction of Copper from Mining Residues by Rhamnolipids

By: Behnaz Dahr Azma

Mining residues, in general, and metal ores, in particular, contain heavy metals within the rock. These heavy metals are very harmful to humans and, as such, are a serious problem for the environment. They can be considered as contaminated rocks. One of the heavy metals with increasing demand around the world is copper (Cu) that is the subject of this study. To extract copper from the residue with 8,950 mg copper per kg rock, a biosurfactant, rhamnolipid was used. To optimize the conditions for maximum extraction, several batch tests were performed on washed ore samples in 25°C. The best size of particle sizes was determined to be between 0.15 and 0.3 mm while the pH was set at 6. A minimum volume of 10mL rhamnolipid of 2% concentration for 1g of ore was required to extract about 28% of copper from the ore. Although better results are also possible with higher concentrations of rhamnolipid, the solution becomes very viscous as well. Adding 1% NaOH to the solution dramatically improved the extraction up to 42% in 6 days. Unwashed samples of mixed size particles were tested under the optimized conditions and 24% of copper was extracted. A sequential extraction procedure was performed to determine the fractions of different forms of copper in the ore. The oxide and hydroxide, residual part, and carbonates are the main fractions and the extracted ore was extracted mainly from the oxide and hydroxide part.

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I would like to express my sincere gratitude to my supervisor Dr. Catherine N. Mulligan for her encouragement, knowledgeable suggestions, and invaluable support in the course of my research.

Also, thanks to Mr. R. Parisella for his help in conducting the laboratory work.

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Chapter 1

Introduction

1.1 General remarks

Metals are part of human life. Heavy metals, metals with specific gravity more than 5, such as copper, iron. lead, and zinc are the first metals that were used by man in his daily life (Neely 1979). “Since the Industrial Revolution, the production of heavy metals such as lead, copper, and zinc has increased exponentially. Between 1850 and 1990, production of these three metals increased nearly 10-fold, with emissions rising in tandem” (WRI 1999). They are found everywhere: soil, water, waste, wood, and food but they are not always useful. The toxicity of heavy metals and especially mercury was known for centuries (Hoekman 2000).

The existence of heavy metals in the environment directly affects living things. For example, mercury effects the gastric and neural systems and even can causes death while zinc, copper, and nickel are harmful to gastric and respiratory systems and also to skin (Sansteed 1977). "Doctors at Loyola University Medical School in Chicago and the Carl Pheiffer Treatment Center have reported that violent males between the ages of 3 and 18 commonly have elevated copper and reduced zinc blood levels when compared to nonviolent males. Depression and schizophrenia also have links to high copper levels" (Hoekman 2000).

Metals can reside in the environment for hundreds of years or more after they are emitted (Hoekman 2000). Natural sources of heavy metals into the environment are not the only ores. Mining of heavy metals and of coal and other minerals, is another major route of exposure since during the extraction process, a part of the heavy metals remains in the ore after discarding. The world mining industry has made some remarkable improvements in worker safety and cleaner production but it yet remains one of the most hazardous and environmentally damaging industries. For example in Bolivia, aquatic life along a 300-kilometer stretch of river systems had been damaged because of toxic sludge from a zinc mine in the Andes as of 1996 which threatened the livelihood and health of 50,000 people in the region. This problem not only affects developing countries, but also it is a major environmental concern in developed countries like Canada. A nickel smelter has devastated 10,400 hectares of forests downwind of the smelter toxic emissions from the Sudbury, Ontario. (WRI 1999)

1.2 Copper

Copper is a metal with atomic number of 29, a molar mass of 63.5g, and a density of 8.9 g/cm^3. Its abundance in the Earth's crust is 0.0007% by mass (O'Conner et al. 1968). Copper is found everywhere: in water, in soil, in plants, in animals, and in food. Copper is also found in yeast and fungi and it is essential for their growth and reproduction. Adequate copper is required for all living things (Owen 1982).

Copper is one of the first metals that man discovered in the form of ore bodies (Banfield 2001). From the beginning of civilization, copper has been continuously discovered and used for many purposes but in 19th century, when the use of electricity and power supply grew, the rate of using copper was grew more rapidly. In 1800, the production and consumption of copper were estimated at 16,200 tonnes per year but at the end of that century it surpassed 450,000 tonnes per year. In 1973, the production was recorded at 8.1 million tonnes and in that year the production for the year 2000 was estimated at 27 million tonnes (Sutulov 1975). This prediction did not come true and the world production of copper in year 2000 stood about 13 million tonnes. Fig. 1-1 shows the production of copper in the last decade of the last century (CDA 2001).

The abundance of copper in the earth's crust changes from one place to another. For example, North America produces around half of the world's copper within it, Arizona is known as "copper state". These deposits of copper may also contain other metals such as gold, silver, and some other intrusive metals (Tatsh 1975).

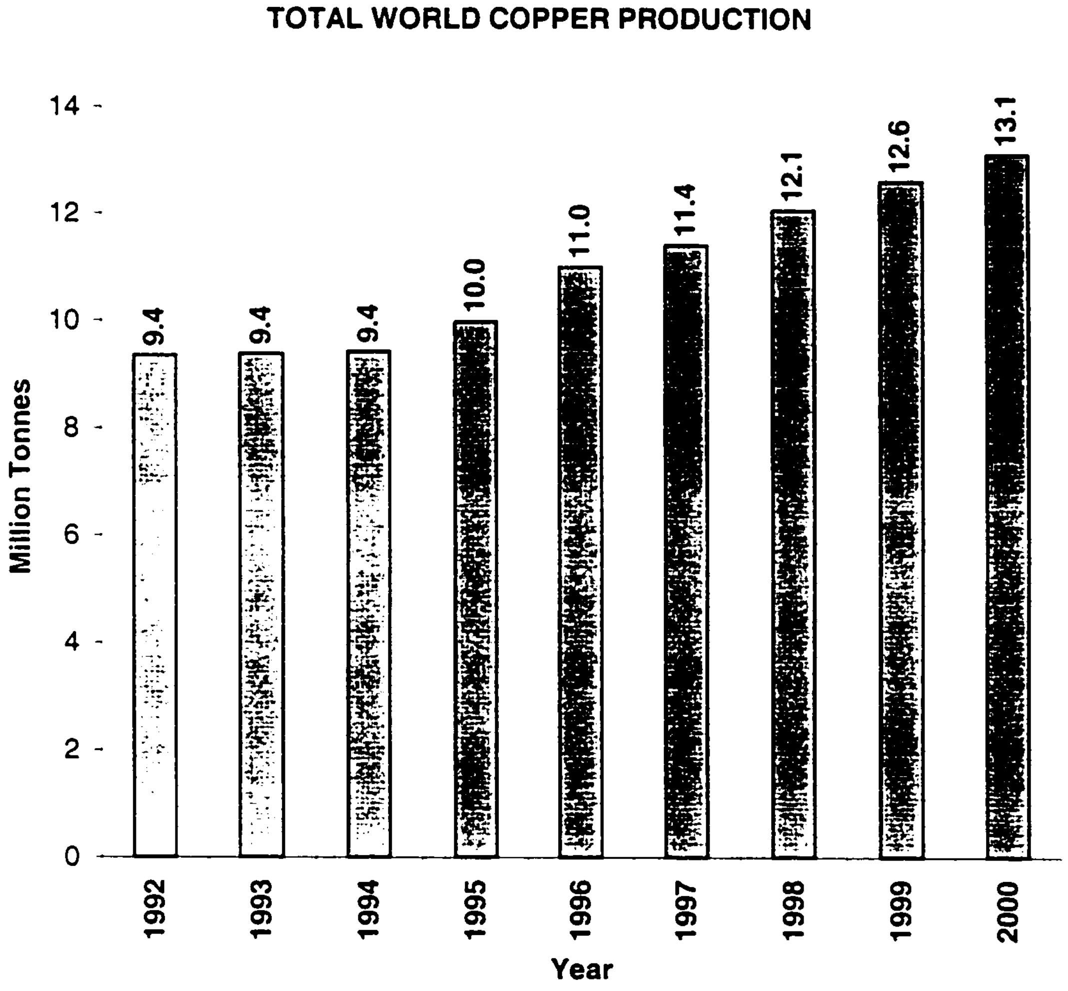


Figure 1-1 **Total world copper production 1992-2000 (CDA 2001)**

Figure 1-2 is a comparative graph that shows the distribution of production sites in the world based on data collected in the year 2000 (CDA 2001).

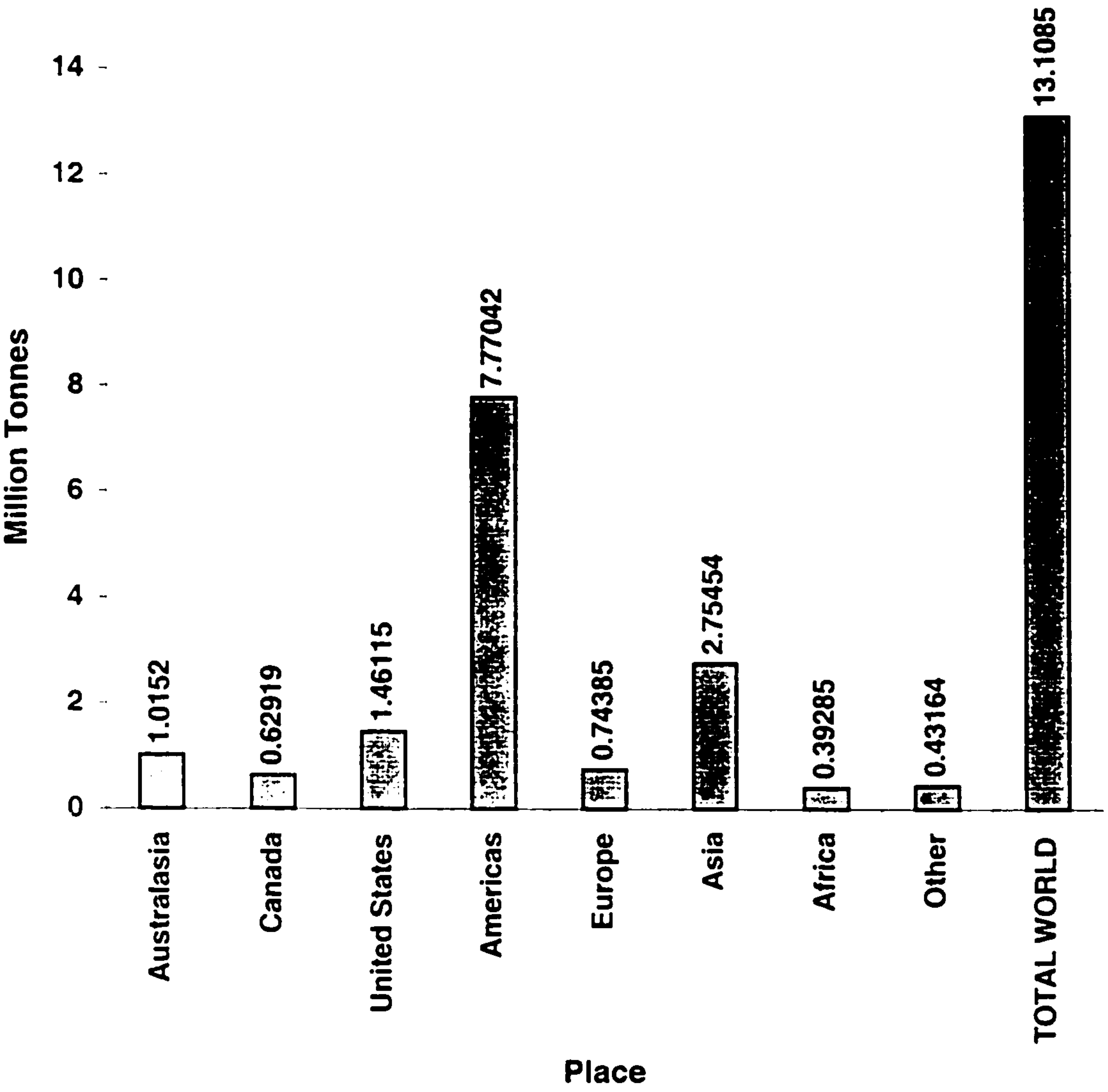


Figure 1-2 Comparative graph of copper production in the year 2000 (CDA 2001)

To cover the rising demand for copper, extraction methods of copper from ore have been improved during the century. Ore is a mineral or aggregate of minerals from which a substance, usually a metal, can be extracted at a profit. In the last century some new industrial methods took part in industry that are based on chemical and biological methods. The biological methods are based on using organic products to change the chemical properties of the ore and release the copper.

In everyday life, copper has a wide range of applications, mostly in electrical devices. Figure 1-3 shows the distribution of copper used in the United States by industries. Although the application of copper in industries does not change rapidly in the sense of plurality, but it raises up by the total weight. For example in the 1970 about 14.2 kg of copper were used in a car but this amount increased by 22.5 to 36.3 kg for a car made in 1995.

Despite the usefulness of metals, they can be harmful to the environment as well as human health. Although all metals do not have the same degree of toxicity, if the concentration of metals in water, food, or even air exceeds that of a standard level, they can cause cancer, mental illness, and bronchial illnesses (Reviewed by Mulligan 1998).

Most metals are toxic at levels of more than 1 or 2 mg/kg tissue (Truhart 1979). Heavy metal control is one of the important goals of environmental engineering. In 1994, in Quebec alone, more than 52 tonnes of copper were released to the soil (Environmental Canada 1996). Copper affects the human gastric system, respiratory system, and skin (source: Governor's office of appropriate Technology, Toxic Waste Assessment Group, California 1981).

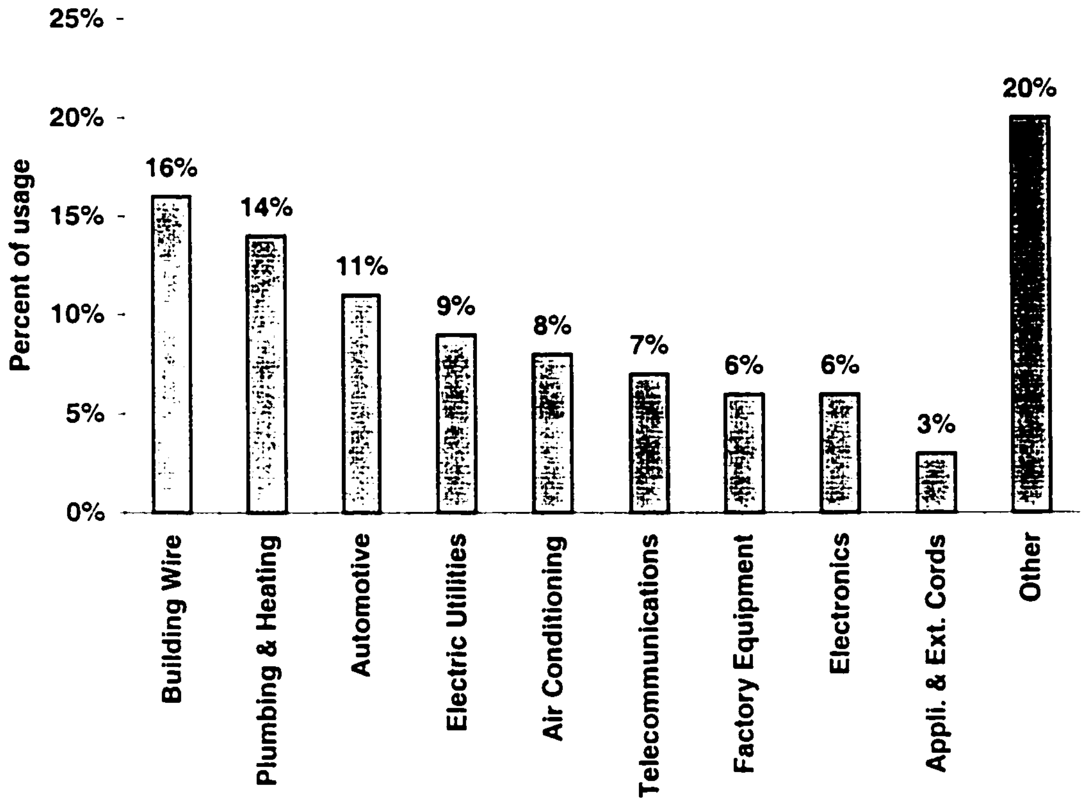


Figure 1-3 **Distribution of the use of copper in USA by industry**

As mentioned above, residues containing heavy metals are considered as contaminated and harmful to the environment. It is necessary to reduce this impact by removing heavy metals from these ore residues. It also is desirable to reduce waste generation.

1.3 Surfactants and biosurfactants

A surfactant is a surface active molecule that has two parts: hydrophilic and hydrophobic. Each part has its own character opposite to the other in the sense of solubility in water (Friberg and Lindman 1992). By this property, surfactants can be applied to soil washing and/or soil flushing processes and also enhance oil recovery and heavy metal removal from contaminated soil (Myers 1992, Mulligan 1998, Holakoo 2001).

Since surfactants have lower toxicity and good biodegradability, they have less effect on the environment than other organic solvents (Deshpande et al. 1999). Some organic byproducts act as surfactants and because of their origin, they are called biosurfactants.

1.4 Objectives

The objectives of this research are as follows:

A. To study the feasibility of using a biosurfactant (Rhamnolipid) in extraction of copper from a low grade mining residue.

B. To optimize the major parameters in extraction of copper from the mining residue.

C. To perform sequential extractions to determine the chemical forms of copper that respond better to the biosurfactant extraction.

To achieve these aims, related literature was reviewed, procedures were designed and appropriate methods and materials were chosen. The results of the experiments are discussed and conclusions were made.

1.5 Organization of the thesis

Chapter One:	The first chapter is the introduction to the thesis. A general overview and the importance of the subject are discussed.
Chapter Two:	Chapter 2 is allocated to the literature review including the history of copper, copper metallurgy, and some common extraction methods used. Some general information on surfactants, particularly rhamnolipids, their chemical and physical properties and applications are presented in this chapter.
Chapter Three:	Procedures, materials, methods, and equipment used in the study are presented in this chapter.
Chapter Four:	Results, obtained data, and preliminary discussion is included in this chapter.

Chapter Five: The conclusion the research, suggested further studies, and the contribution to the knowledge are presented in chapter five.

References are presented as the last part of the thesis.

Chapter 2

Literature review

2.1 Heavy metals and copper extraction

2.1.1 General remarks and brief history

Metals are common elements in the Earth. They can be categorized in different ways as heavy metals (iron, copper, tungsten, zinc,..), light metals (aluminum, lithium, magnesium,..), white metals (lead, tin, zinc,..), and precious metals (gold, silver, platinum palladium,..) but qualitatively they can be defined as chemical elements with characteristics of heat and electrical conductivity, lustrous appearance, and malleable behavior (Clark and Varney 1962). Metals, whose densities of the elemental form are higher than 5000 kg/m^3, are called heavy metals (reviewed in Nies 2001).

Extraction of metals from their natural sources is a general expression for a wide range of engineering processes, metallurgy. It is believed that the history of metal extraction started after man used fire for his needs. The art of smelting was discovered toward the end of Stone Age and after that the first crude bronze was made as a result of accidental roasting of mixtures of copper and tin ore. This accidental exploration, led man to a new age: the Bronze Age in 2500 BC. After that brass, another alloy of copper, was discovered and the Brass Age started around 500 BC (Clark and Varney 1962).

Metals in general and copper, in particular, are highly important to man. Copper deposits are classified into five groups (Tatsch 1975):

1) Porphyry, vein, and replacement deposit (65%).
2) Sedimentary rocks (25%)
3) Massive sulfide deposits in volcanic rocks (5%).
4) Nickel-copper ores formed by magmatic processes.
5) Native copper of the Keweenaw type.

Regardless of which type the ore is, the extraction process depends on the chemical compounds that contain copper. Some common minerals of copper are cuprite, azurite, malachite, and native copper.

2.1.2 Methods of extraction

Metallurgy is defined as "the technology of extracting metals from their ores and refining them for use and the science or study the behavior, structure, properties, and composition of metals" (Neely 1979). It is also known as the science and art of preparation and application of metals and alloys (Clark and Varney 1962). Metallurgy is usually divided into three fields: chemical metallurgy, physical metallurgy and mechanical metallurgy (Clark and varney 1962).

- Chemical metallurgy includes processes involving chemical reaction on the ore to extract or purify metals.
- Physical metallurgy includes physical processes such as heating, cooling, and so on to change the physical properties of metals.
- Mechanical metallurgy is the use of mechanical processes including tension and torsion to improve the mechanical and physical properties of metals.

Since this research deals with chemical metallurgy, from this point, our concern in the literature review will be on this subject. Chemical metallurgy by itself is divided into three major methods: pyrometallurgy, hydrometallurgy, and electrometallurgy. In the next section, these three methods are reviewed.

2.1.2.1 Pyrometallurgy

In this method heat is used to smelt the metal and extract it from the other parts of the ore. This method is the first extraction method developed and is still very common especially in iron extraction. All of the old metal factories operated with this method. The rise in the price of fuel required to provide the necessary heat and mixing to bring the metals close to the melting temperature is the major economic concern that led to the use of other methods.

2.1.2.2 Hydrometallurgy

As its name implies, hydrometallurgy is a wet method in that the ore is put in a wet environment with a mostly aqueous solution. The method is based on the solubility of metals in solvents used to extract precious metals from ore. It is, however, a costly method.

Hydrometallurgy has a history in analytical chemistry where chemists tried to separate one metallic ion from another. Hydrometallurgy was used first in a large-scale, during World War II for the recovery of uranium from its ores. The key to the process is finding the right organic extractants to provide appropriate conditions in the ore for extraction (Dresher 2001 a).

The history of mining in Nevada gives a good example of using hydrometallurgy. In Nevada, sodium cyanide solution is used to extract silver and gold from the rock. The process starts with placing the sodium cyanide solution on a rock heap. The solution dissolves the silver and gold and the draining fluid that contains metals and solution is collected. This fluid is called pregnant since it carries metal ions. The material used in process is the residue of ore that had been processed with the old extraction method using mercury. In the 19th century, in Nevada, gold, silver and other metals were found in high percentages. At that time the extraction method was based on amalgam process that released more than 6300 tonnes (by some estimates) of mercury to the Carson River downstream from the mills and also left 15-40% of the silver and gold in the ore residue. Mercury is still used in many Third World countries to treat precious metal ores. The use of cyanide is a good example of a hydrometallurgy process. Cyanide can be rapidly degraded into carbon and nitrogen in sunlight or in contact with the atmosphere (Lugaski 1997, Newton 1959).

In some cases a biological process using fungi that produce chemical extractants is used in the hydrometallurgy method. This method is called bio-hydrometallurgy. If the problem of nutrition needed for the fungi is solved at a reasonable cost, this method can become significant (Kamali 2001). As a matter of fact this method is already being used successfully at a small scale and a promising future for this method is predicted. A detailed review of the application of microorganisms in the copper metallurgy is presented in section 2.2.5.

2.1.2.3. Electrometallurgy

Electrometallurgy is a metallurgical method to purify the extracted metal by pyrometallurgy and/or hydrometallurgy. It is not considered as a comprehensive method to be applied to the metal ore. In this method a DC current is applied to the two poles, electrodes, that are placed in a solution called an electrolyte. The DC current acts on the metals, creating a flow of metal ions from one electrode to another. Depending on the primary treatment, the metal could be in metallic or ionic form. The metal obtained from this method is considered commercially pure. Almost all pure copper in the market and also all gold and silver are extracted by an electrometallurgy process (Newton 1959).

2.1.3 Copper extraction and copper metallurgy

Copper is one of the most common heavy metals and is found in several natural forms. In some deposits, copper is the main metal extracted but it is also found in some other ores, which are rich in other metals and low in copper. Like other metals, copper undergoes several processes from the ore to the commercial product. This process is different for various ores as the ore properties change from one deposit to another. In this section a general description of copper ore processing is presented. The electrical treatment of copper is a part of both pyrometallurgy and hydrometallurgy of copper and is described within those processes.

2.1.3.1 Copper pyrometallurgy

Copper pyrometallurgy, like pyrometallurgy of other ores, is a process based on heating the ore (pyro = fire). Before the process starts, the ore should be prepared and purified as much as possible. The majority of copper ore comes from open mines with the exception of a few places such as Australia, where all copper comes from underground mines and in Manitoba, Canada. The mining process in open mines is as simple as ordinary excavation and, therefore, open mines are less expensive as compared to underground mines (MEM 1986).

The second step is grinding and powdering of the ore. In this step, the ore is milled and becomes powder. Generally, a fine powder results in good separation between particles carrying copper and those that do not contain copper. The remaining particles are called gangue.

The next step in ore refining is floatation that includes separation of ore grains from dust and waste material. Floatation includes putting the ore powder in water in the presence of some reagents that wet all particles completely (CE 2001). The wetted particles are blown by compressed air and those particles, which contain sulfides of metals, float and come to the surface. Then the froth is collected, filtered, and may be dried. The product is called copper concentrate. Copper refineries are usually very close to the mines to avoid unnecessary transportation cost that is remarkably high since the excavated material contains about 90% waste (MEM 1986).

Smelting is the next step in pyrometallurgy. In this step the concentrated copper is heated until it becomes melted. In the heating process the reaction occurs as shown in equation 2-1:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \qquad [2\text{-}1]$$

The product of this process is called matte. Depending on the location and the other materials in the ore, the obtained matte contains between 25% to 57% copper (MCA 2002). The next process for the copper matte is the converter. In this step, the pure copper is extracted from its chemical components [Eq. 2-2].

$$Cu_2S + 2\,Cu_2O \longrightarrow 6Cu + SO_2 \qquad [2\text{-}2]$$

The resulting copper is called blister copper and is ready for final refining. The blister copper contains about 98 to 99 per cent metallic copper. In both reactions above the quantity of the resulting material on the right hand sides of the equations depends on the temperature and the size of the material. The first reaction (2-1) provides 770 kJ while the second reaction (2-2) needs 117 kJ (Newton 1959).

Although the blister copper is almost pure, it is not ready for market yet. Almost all copper produced from ore receives an electrolytic treatment for purifying either in the electrofining process. This is the last step in the pyrometallurgy or electrowinning in hydrometallurgy. Electrofining is a more common process than electrowinning since pyrometallurgy is common extraction method. By some data, cathode copper from electrofining is 95% of all world copper production while the electrowinning produces only 5 percent (Scheikunde 2001).

In the electrofining process, the copper has to be refined in an anode furnace and finally purified by electrofining. The final product contains 99.99% copper and is commercially pure (MCA 2002).

In general, the electrofining process has two major purposes:

1. Elimination the unwanted impurities; cathode copper typically has a purity > 99.9 % wt Cu, with < 0.005 % total metallic impurities;
2. Separation of valuable impurities which can be recovered in other processes.

The electrofining process for copper is usually carried out in aqueous solution where the electrolyte is copper sulfate (0.7 M) and sulfuric acid (2 M).

According to the London's Metal Exchange Market, the price of one tonne of "Grade A Copper" for January 2002 was about $1500 USD. This means copper is considered as a valuable metal which is a reason for the numerous research studies on copper extraction (Felsher et al. 2000).

2.1.3.2 Copper hydrometallurgy

In the hydrometallurgical method, the copper ore is first broken and placed on special concrete vats that are covered by acid-resistant material. The solvent is added onto the top of the ore. This solvent dissolves the copper and the solution is collected for the next process. The solvent continuously cycles until all copper dissolves or the extraction of the remaining copper is not economic.

In the conventional method of hydrometallurgy, the leaching agent or solvent, is a solution of 25 to 80 g of free sulfuric acid in water. The ore is washed with a series of weak solution and finally with fresh water (Newton 1959). Although hydrometallurgy was first used for extraction of copper from copper oxides, today it is used for all kinds of copper ores. The use of hydrometallurgy has increased in world copper production after the 1950s (Dresher 2001 a & b and MCA 2002). It has been improved and today it is usually known as solution exchange electrowinning or "SX-EW" process.

The first extractant that was specifically introduced for copper and used on a commercial scale was LIX 64®. This was a General Mills Corporation product and for the first time Ranchers Exploration and Development Corporation demonstrated it on a large scale at its Bluebird Mine in Arizona in 1968. The SX-EW process as mentioned, involves two stages of solvent extraction and electrowinning (Dresher 2001 a).

A. Leaching (SX)

Depending on the chemical formulation of the copper ore, different chemical reactions may happen in the leaching vat. Here, some of the most frequent reactions are presented. The first stage, solvent exchange (SX) starts with leaching the material with a weak acid solution (Newton 1959).

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad [2\text{-}3]$$

Sometimes it needs a ferric salt to be dissolved:

$$CuS + 2FeCl_3 \longrightarrow CuCl_2 + 2FeCl_2 + S \qquad [2\text{-}4]$$

$$Cu_2S + 2FeCl_3 \longrightarrow 2CuCl + 2FeCl_2 + S \qquad [2\text{-}5]$$

$$3CuO + Fe_2(SO_4)_3 \longrightarrow 3CuSO_4 + Fe_2O_3 \qquad [2\text{-}6]$$

$$Cu_2S + Fe_2(SO_4)_3 \longrightarrow CuS + CuSO_4 + 2\ FeSO_4 \qquad [2\text{-}7]$$

$$CuS + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2\ FeSO_4 + S \qquad [2\text{-}8]$$

This solution, or the pregnant liquor, is recovered and then in the next step is coming in mix with an organic solvent, called extractant. In the first stage, copper is extracted from the aqueous phase and most of the impurities that exist in the leach solution are separated from the copper containing materials. An environmentally important fact in this stage is the return of the aqueous phase to its original acidity and recycle to the leaching step since the copper ion is exchanged for the hydrogen ion. At the same time the copper bearing organic phase loses the copper in the presence of a strongly acidified aqueous solution. Then the copper is moved to the aqueous phase while the organic phase is reconstituted in its hydrogen form. The copper-bearing aqueous phase is the raw material for the next stage or electrowinning (EW).

B. Electrowinning (EW)

The second stage of the process, EW, is to reduce copper from copper sulfate in solution to a metallic copper cathode through an electrochemical process. Copper that is obtained from the electrowinning process at the cathode is as pure as or purer than that collected in electrorefined cathodes from pyrometallurgy. That may explain why it is well received by the market (MCA 2002).

An energy comparison between pyrometallurgy and hydrometallurgy shows that there is a remarkable difference between these two methods. The pyrometallurgy process requires around 65 MJ/kg ore (not including scrap recycling) while the SX/EW process requires about 15 MJ/kg (from heap or dump leaching) to 36 MJ/kg (from mined and crushed ore). The variation in energy consumption not only depends on the materials, but also on the site plan of the installations. For example, the required energy for pumping the liquid materials in the United States is estimated to vary from 10 MJ/kg to 25 MJ/kg (Drosher 2001 a).

Although the pyrometallurgy processing of copper needs more energy than the hydrometallurgy, the required energy in the last stages, which are electrofining and electrowinning shows another aspect: 8 MJ/kg for electrowinning vs. about 1.5 MJ/kg for electrorefining. The main difference between electrowinning in hydrometallurgy and electrofining in pyrometallurgy is the form of copper. In electrofining, copper comes from the smelter or roaster. It is already in the metallic form and is merely transported from the anode to the cathode to purify it while in electrowinning, the copper is in a cupric state.

An important advantage of hydrometallurgy is the lower initial investment, compared to pyrometallurgy. It is also possible to run a hydrometallurgy plant in a small scale economically. This property makes this method very suitable for small deposits.

Since in this method, the solvent acts on the desirable part of the ore, but in smelting all impurities in the concentrate are heated, this makes hydrometallurgy more profitable for low grade ores.

2.2 Surfactants

Surfactant is an abbreviation for " **surface active agents**". They are also called surface active substances and surface active compounds (Tsujii 1998). These materials are able to lower the surface tension of a solvent. Meanwhile they form aggregates, micelles, in aqueous media (Myers 1999). This property is very important, as their effectiveness depends on their ability to reduce surface tension (Rosen 1978). An effective surfactant is able to reduce the air-water interface to 35 mN/m and the oil-water interfacial tension to 1 mN/m (Mulligan and Gibbs 1993).

Surfactants are defined as amphiphilic compounds, meaning that they contain both hydrophobic and hydrophilic portions (Fig. 2-1). They have the ability to replace the bulk molecules of higher energy at an interface to reduce the free energy of the system. The important characteristic of surfactants is that the hydrophobic portion has little affinity for the bulk medium while the in hydrophilic portion is attracted to the bulk medium (Mulligan 1998).

Surfactants are used in a wide range of applications in industry. They have been used as adhesives, flocculating, wetting, and foaming agents (discussed in Mulligan 1993).

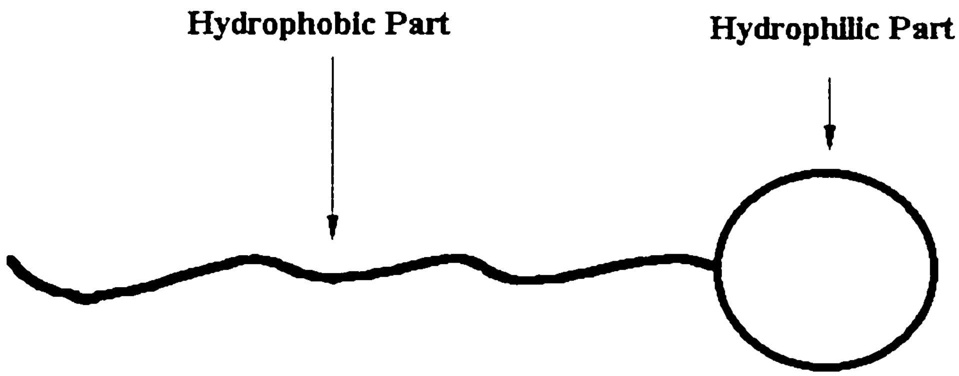


Figure 2-1 Surfactant structure (Adapted from Myers 1999)

2.2.1 Characteristics of surfactants

Surfactants have three important characteristics: surface tension, hydrophobic-lipophilic balance or HLB, and critical micelle concentration or CMC. In this section a brief review of each is presented.

"The attraction between molecules forms an imaginary film capable of resisting tension at the interface between two immiscible liquids or at the interface between a liquid and a gas. The liquid property that creates this capability is known as surface tension" (Daugherty et al. 1989). This is the definition of surface tension from a fluid mechanics point of view. With a look to the molecular and atomic arrangement of fluid, we will find the reason for the existence of such tension. In a liquid, each molecule interacts with the interactive forces of surrounding molecules. At the surface these forces are absent or negligible and thus those molecules have excess energy compared to those in the bulk of the liquid. This excess energy is defined as the surface tension (Tsujii 1998).

The next characteristic of a surfactant is HLB. As mentioned above HLB is the abbreviated form of hydrophilic-lipophilic balance. HLB is the number that represents the tendency of a surfactant to dissolve preferentially in oil or in water as discussed in Mulligan and Gibbs (1993). This value changes from 1 to 20 for the most lipophilic to the most hydrophilic respectively (Kunieda and Sato 1992 and Tsujii 1998).

The CMC can be defined as the minimum concentration of surfactant at which micelles formation initiates. By increasing the surfactant concentration, the surface tension decreases until it reaches CMC. Beyond this level of surfactant concentration the surface tension remains constant. Figure 2-2 shows a typical CMC, derived from a plot of the surface tension versus logarithmic surfactant concentration.

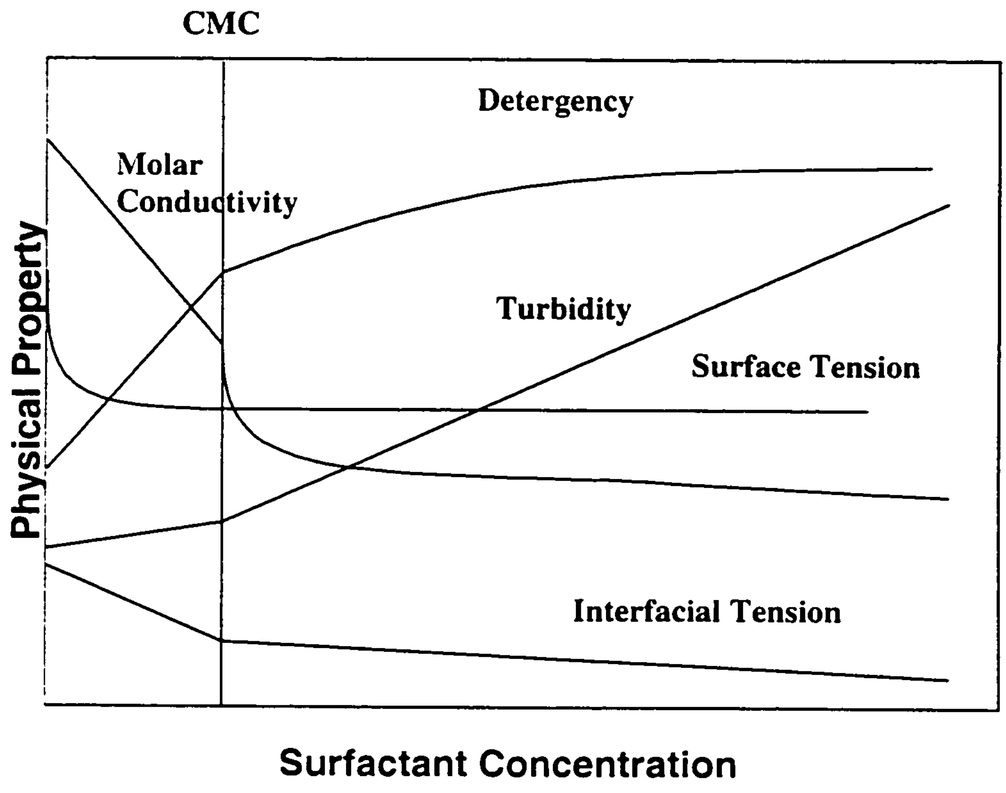


Figure 2-2 Variation of some important physical properties by surfactant concentration (Adapted from Myers 1992)

It is well known and described in the literature that low CMC values represent a more efficient surfactant since less surfactant is needed to decrease the surface tension (Becher 1965 and Mulligan 1998). Figure 2-3 shows the mechanism of arrangement of surfactant molecules in two cases: below and above the CMC.

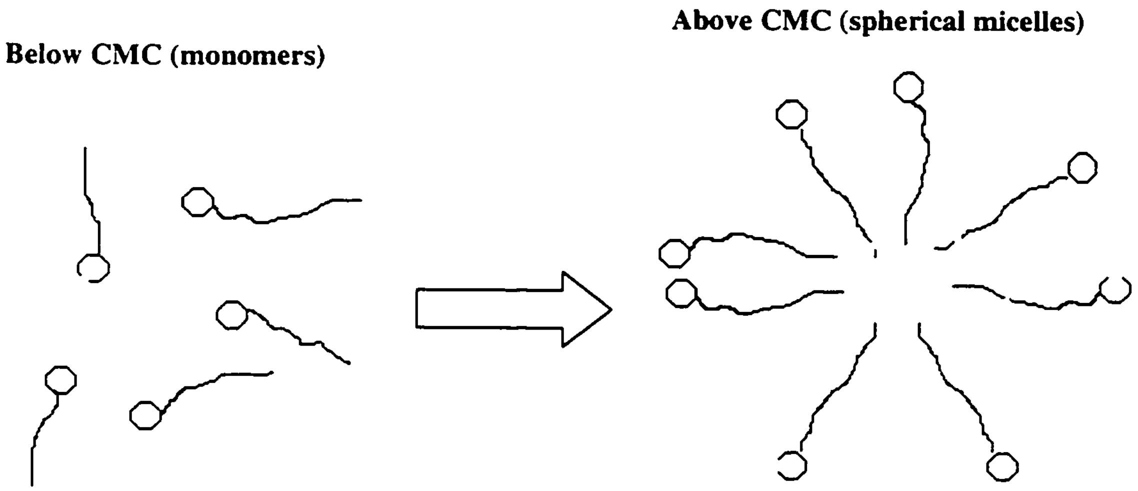


Figure 2-3 Surfactant Micellization (Adapted from Becher 1965)

2.2.2 Types of surfactants

Surfactants are classified into four groups: anionic, cationic, amphoteric, and nonionic. This classification is based on their hydrophilic groups that contain anionic, cationic, amphoteric, or nonionic portions, respectively (Fig. 2-4). Surfactants in each group are used for particular purposes. In general, anionic surfactants are mainly used in detergents while amphoteric surfactants are used as boosters to enhance the detergency and/or foaming of them. Cationic surfactants are used in fabric softeners and hair conditioners. Nonionic surfactants are the choice for washing oily dirt and also as emulsifiers (Tsujii 1998).

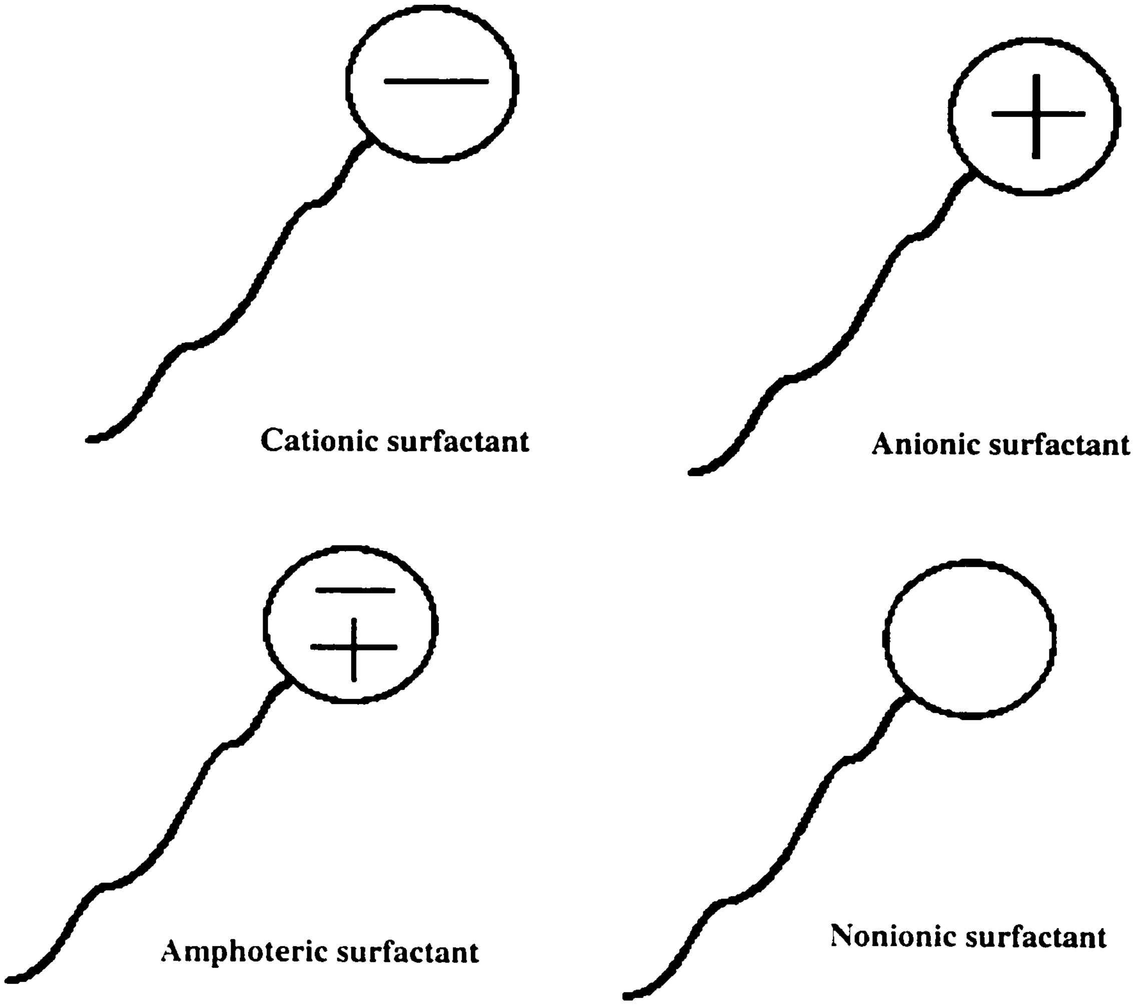


Figure 2-4 Types of surfactants (Adapted from Myers 1992)

The most important selection criteria for surfactants are charge type, physicochemical behavior, adsorption behavior, and solubility (Oberbremer et al. 1990).

2.2.3 Biosurfactants

Biosurfactants are a group of surface active agents naturally produced by certain types of microorganisms. They have a two-portion structure of hydrophilic and hydrophobic parts, similar to the synthetic surfactants (Ju 1999).

Surfactants show some level of toxicity to microorganisms because they can be adsorbed at interfaces. This interaction between the hydrophobic part of a surfactant with the proteins in cell membranes can solubilize components of membranes with a very high protein-lipid ratio . This affinity lowers the cell activity by decreasing the enzyme activity. Hunt (1994) mentions that such an interaction between surfactant and cell causes a level of toxicity.

Since biosurfactants show a very low level of toxicity, they have been considered as a substitution for synthetic surfactants for the last few decades. New biotechnological methods provide inexpensive ways to manufacture biosurfactants at large scale decreases the price of these products and makes them more economical to use widely in industry.

Although the low level of toxicity is a big advantage of biosurfactants over synthetic surfactants, it is not the only one. Other remarkable advantages of biosurfactants are:

- Small in size: biosurfactants have smaller sizes and smaller molecular weights (less than 1500).

- Increased biodegradability

- Effectiveness: they are effective at extreme conditions over a wider range of temperature, pH, and salinity.

- Ease of synthesis: biosurfactants are made by microorganisms rising the possibility of in-situ production (Muller-Hurtig et al. 1993, Ju 1999) since they are synthesized as metabolic by-products (Mulligan and Gibbs 1993). "The composition and yields depend on the fermentor design, pH, nutrition composition, substrate, and temperature used (Mulligan 1993)".

Biosurfactants have been found useful in various fields such as crude oil drilling, pharmaceuticals, and food processing industries (Ju 1999, Muller-Hurtig et al. 1993, and Fietcher 1992).

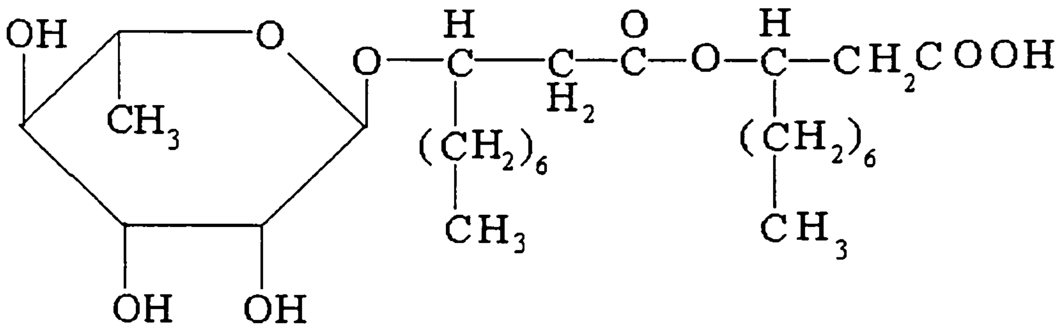
2.2.4 Types of biosurfactants

Biosurfactants include glycolipids, lipolipeptides, phospholipids, fatty acids, and neutralipids (Tsujii 1998, Biermann et al. 1987). The majority of biosurfactants are anionic or nonionic and only a small group of them such as those that contain amine functions are classified as cationic. Their CMC varies between 1 to 200 mg/L and molecular their weights are between 500 to 1500 (Lang 1987).

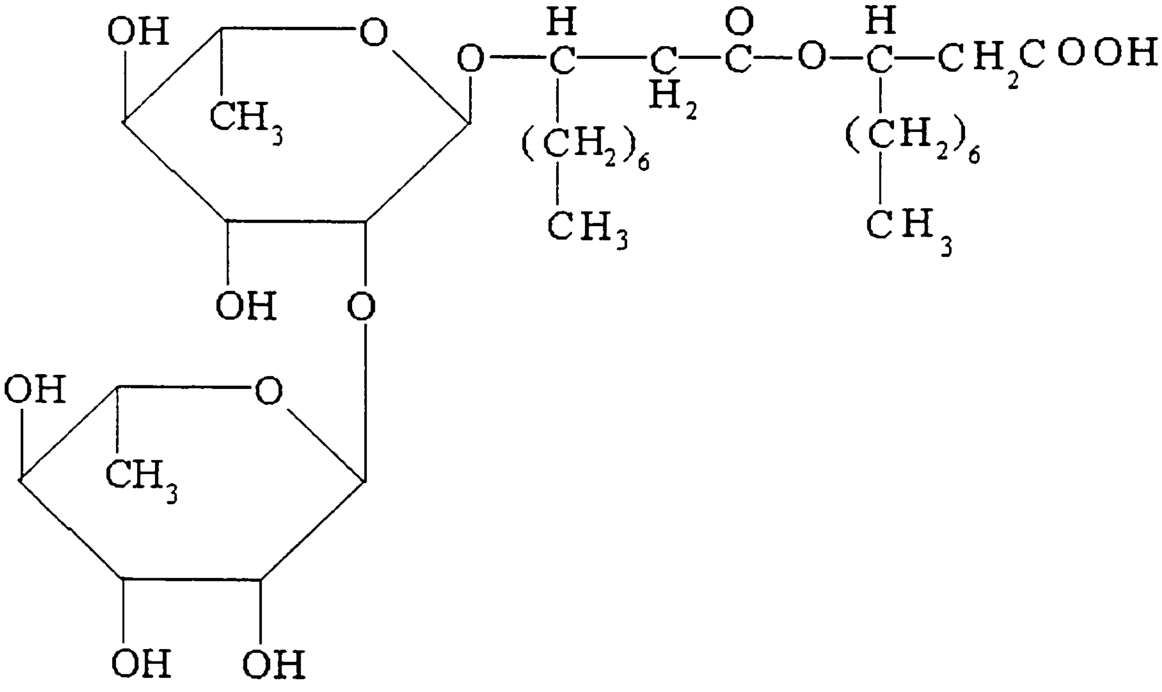
Rhamnolipids, used in this study, are biosurfactants from the glycolipid group made by *Pseudomonas aeruginosa*. The relationship between rhamnolipid and *Pseudomonas aeruginosa* is very special. *Pseudomonas aeruginosa* produces and releases rhamnolipid for emulsification of n-alkanes to transfer them to its cells. Rhamnolipids are active only in the case by assimilation of *Pseudomonas aeruginosa*. Other kinds of glycolipids do not show such a behavior and they are not so specific for the species of microorganisms (Hitsatsuka et al. 1971, Tsujii 1998)

There are four types of rhamnolipids and their chemical structures are shown in Figure (2-5) (Tsujii 1998). Rhamnolipid type I and type II are suitable for soil washing and heavy metal removal while type III is for metal processing, leather processing, lubricants, pulp and paper processing. Type IV is usually used in textiles, cleaners, foods, inks, paints, adhesives, personal care products, agricultural adjuvants, and water treatment (Jeneil 2001).

The physical characteristics of rhamnolipids have been reported by several investigators. The physical properties and the range of variation is presented in Table 2-1 (Mulligan and Gibbs 1998, Thangamani and Shreve 1994, and Zhang and Miller 1995).

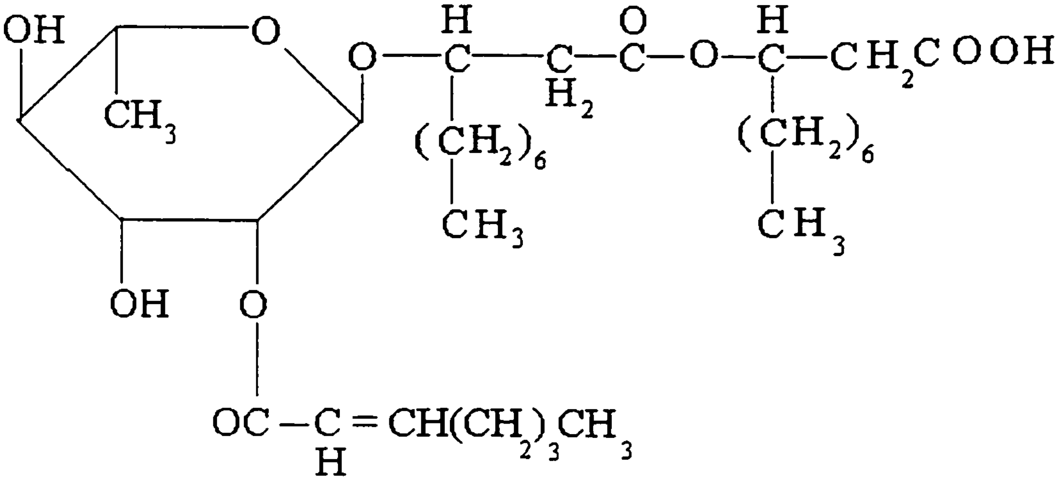


Rhamnolipid Type I

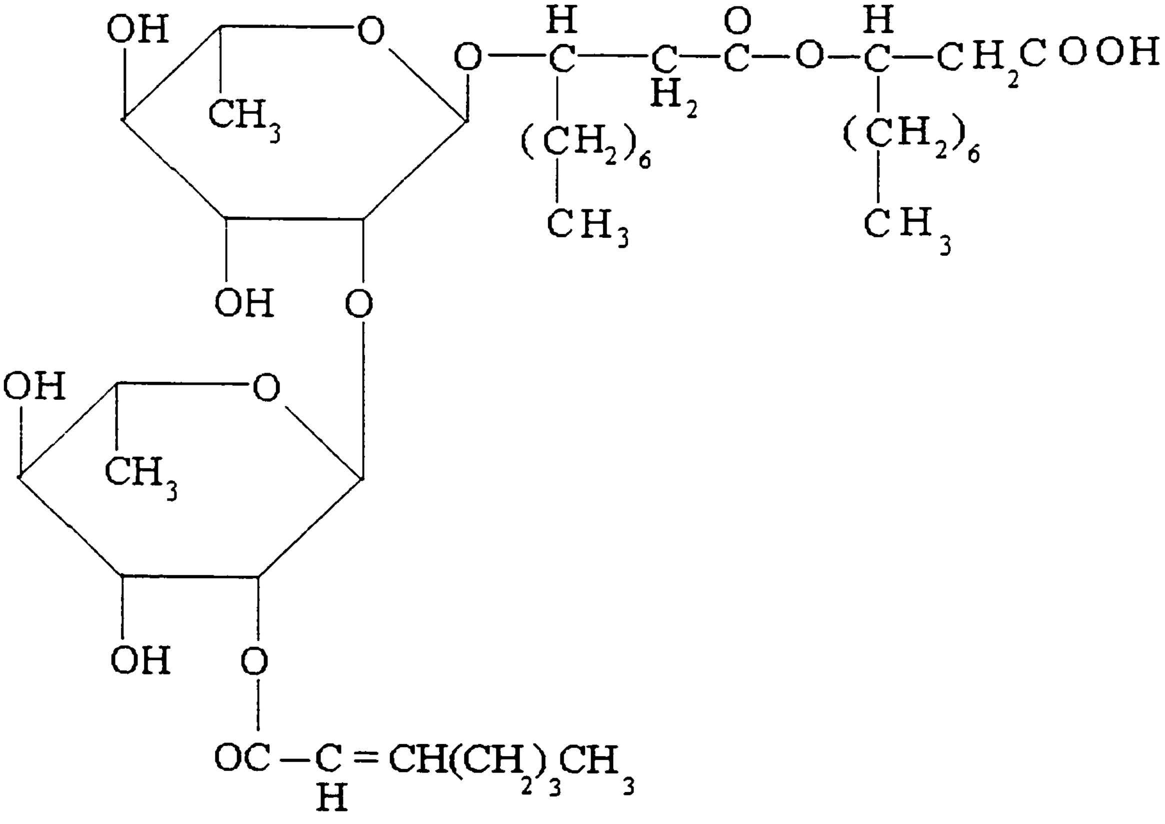


Rhamnolipid Type II

Figure 2-5 Different types of rhamnolipids (Adapted from Tsujii 1998)



Rhamnolipid Type III



Rhamnolipid Type IV

Figure 2-5-cont'd Different types of rhamnolipids (Adapted from Tsujii 1998)

Rhamnolipids like other surfactants can lower the air/water surface tension. For example, for distilled water the surface tension is lowered from 72 mN/m to around 30 mN/m in the presence of rhamnolipids (Zhang and Miller 1992).

Rhamnolipids can also enhance soil flushing efficiency and the rate of adsorption of heavy metals from soil. This ability makes them suitable to remove heavy metals from soil to reduce the toxicity of soil. The same concept is used to extract metals from ore, by almost the same mechanism. A detailed discussion on the latter purposes will be presented in the next section.

Table 2-1 Some physical properties of rhamnolipids

Physical Property	**The range of variation**
Average surface tension	**29 - 40 mN/m**
Micelle diameter	**5 nm**
CMC	**25 – 60 mg/L**

2.2.5 Biohydrometallurgy

Microbial leaching is a hydrometallurgical process involving metabolic activities or products of organisms. The basis of this method is very simple: an organism or a group of organisms are used in leaching and the method is called bioleaching (Kamali 2001 and Rossi 1990).

The idea is not new and has been in use for more than 2000 years (Rossi 1990) but the method is not used at a commercial scale widely because of the cost, and efficiency (Kamali 2001).

Two types of microbial leaching have been developed: chemolithoautotrophic leaching and heterotrophic leaching. A brief review of both methods will be presented in the following subsections.

2.2.5.1 Chemolithoautotrophic leaching

The term chemolithoautotrophic defines a special kind of autotrophic organism which use the oxidization of sulfur as a source of energy. Most of these microorganisms are bacteria of the *Thiobacillus* type.

The role of bacteria in the formation of acid mine drainage from pyrite was reported in 1950 for the first time (Kamali 2001). Following the first report, several studies were performed and until now, two types of bacteria were found in different types of copper sulfide mineral mines: *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans.* Both of these bacteria are widely used in bioleaching at commercial scale (Brandl 2001). The optimum conditions for growth and reproduction of these bacteria are a temperatures between 25 – 30°C and a pH of 1.5 to 2. Therefore, they are classified as mesophilic and acidophilic bacteria (Kamali 2001).

The source of energy for *Thiobacillus ferrooxidans* is from either ferrous iron or reduced sulfur compounds while *Thiobacillus thiooxidans* gains energy only by oxidation of reduced sulfur compounds. Both bacteria decompose mineral sulfides in pure culture.

The reactions are basically the conversion of the insoluble form of the metal to a soluble form through microbial oxidation of metal sulfides (Ehrlich 1999). The following equations describe the "direct" and "indirect" mechanism for the oxidation of:

Direct:

$$2FeS_2+7O_2+2H_2O \longrightarrow 2FeSO_4+2H_2SO_4 \qquad [2\text{-}9]$$

Indirect:

$$4FeSO_4+O_2+2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3+2H_2O \qquad [2\text{-}10]$$

$$FeS_2+Fe_2(SO_4)_3 \longrightarrow 3FeSO_4+2S \qquad [2\text{-}11]$$

$$2S+3O_2+H_2O \longrightarrow 2H_2SO_4 \qquad [2\text{-}12]$$

However, the model of “direct” and “indirect” metal leaching is still under discussion (Brandl 2001).

2.2.5.2 *Heterotrophic leaching*

This process mainly focuses on the leaching of oxide ores (prevalent type of ore). Two theories were established to explain the mechanism of this process:

i. A strong inorganic mineral acid with very low pH, such as sulfuric acid, exchanges the hydrogen ion with the divalent metal cation from the ore.

ii. Microorganisms produce some compounds that are able to seclude metals into soluble complexes through chelation.

If a microorganism generates organic acids, a combination of both mechanisms occurs.

One of the main types of microorganisms involving in leaching are fungi. Since fungi are food consumers, fungal leaching is categorized as hetrotrophic leaching. There are some concerns as well as some positive points about using fungi in bioleaching (Kamali 2001):

- They need a considerable amount of organic carbon.
- The leaching process by fungi takes more time than by bacteria such as *Thiobacillus.*
- Fungi are capable of using inexpensive organic wastes as an organic carbon source.

- They form complexes of metal ions that are more soluble in neutral environments with low toxicity.

Kamali (2001) reports a maximum 68% of copper dissolution as well as 46% of zinc, 34% of nickel and up to 7% of iron co-dissolution with *A. niger.* The sources of organic carbon for this research are different food and agricultural wastes such as potato peels, sawdust, and sucrose.

2.2.5.3 New developments in biohydrometallurgy

Biosurfactants, as byproducts of bacteria, have shown some capability in the removal of heavy metals and oil from contaminated soil (Mulligan 1998). Although no independent research on heavy metal extraction using biosurfactants has been reported, the potential capability of such a process can be considered. The present study makes the first contribution to this subject.

2.2.5.4 Bioleaching in Canada

In Canada this method was initiated during the 1970s and 1980s but only one commercial plant uses this technology. "Bioleaching has the potential in Canada to exploit low-grade, remote resources in an environmentally sensitive way. Some observers in the industry believe that, with modest improvements in technology (i.e. by increasing the kinetics and efficiency of the process under conditions specific to the climate in Canada) as many as 10 new mineral deposits could be exploited in this way within the next 10 years" (CANMET 2002).

Canada is one of those countries that are pioneers in mining biotechnology but in the mining industry inside Canada, very few biotechnological processes are used. For example bioleaching has found only two commercial applications in this country: a uranium bioleaching facility at Denison Mines and a secondary copper heap bioleaching facility in Gibraltar, British Columbia (Industry Canada 2001). The main reasons for this ignorance of bioleaching in Canada:

- Conventional processing technologies such as roasting and smelting produce more than enough to met the demand that caused an overcapacity in Canadian copper industry. Canadian companies have been adopting bioleaching technology in other parts of the world such as Chile, where there is no overcapacity (Industry Canada 2001).
- Conditions specific to the Canadian climate. The majority of methods adopted are for temperatures between 15 to 55°C (Mulligan 1998) thus requiring additional energy costs.
- The copper industry perceives that biological processes are not reliable since the bioleaching process did not meet expectations when it was first tested in Canada (Industry Canada 2001).

There is a demand to adapt these biometallurgical methods to the Canadian climate and more research is necessary.

2.3 Sequential extraction

Heavy metals including copper are found in several chemical forms in different ores. Sequential extraction is related to the distribution of the metal, in this case copper, in its different chemical forms.

By using sequential extraction, one can determine which metallurgical method is more efficient for any kind of ore. In the case of using biosurfactants for metal extraction, sequential extraction determines which part of the ore the biosurfactant is removing. It also can be used to interpret the difference in efficiency of the same biosurfactant or any other extractant on different ores.

The importance of sequential extraction is not limited to metallurgical purposes but it is also a powerful tool in environmental sciences as well because this technique can show the source of heavy metal contaminants. It is also possible to determine which forms of the heavy metals have a better chance of mobility.

The technique is not standardized (Mulligan 1998) but in general as its name indicates, it has several steps. In each step a reagent is used and some forms of the metal that are soluble in the reagent are extracted. Finally, a mineral acid is used to digest the residue. The importance of the latter step is to close the mass balance. The concentration of the extracted metal in each step can be determined by atomic adsorption or other techniques.

Since the method is not standardized, the results vary according to the extractants used. The main concern, therefore, will be to find proper reagents that extract a particular form of metal with minimum solubilization of the other forms present in the ore. Comparing the results of sequential extraction before and after applying the (bio) surfactant shows which form of the metal, in this case copper, is being extracted.

The fractions of a metal are categorized as five groups: soluble, exchangeable, organic, oxide, and residue. For each group a special treatment is necessary as follows:

- Water and surfactant extract the soluble fraction.

- Ammonium acetate, barium chloride, or magnesium chloride at pH 7.0 is commonly applied to the ion exchangeable part. Their electrostatic attraction causes the ion displacement in the ore matrix (Lake 1987). Among the reagents mentioned above, magnesium chloride leaches low quantities of other metals in the form of sulfides, organic matter, aluminum, and silicate (Pickering 1986).

- To extract the carbonate fraction (calcite and dolomite), sodium acetate is used. The pH is lowered to 5 by acetic acid.

- The next step is the extraction of copper from the organic matter. Hot hydrogen peroxide is used to oxidize the organic matter and solubilize the sulfides. The advantage of this reagent is that it does not affect silicon.

- A strong acid is used to dissolve the silicate and other forms of metal in order to closure the mass balance.

It should be mentioned that investigators recommended different steps and procedure that are slightly different from one anothers (Chao 1983, Gatehouse et al. 1977).

Chapter 3

Methods and materials

3.1 General remarks

The aim of this study is to extract copper from ore by using biosurfactants. To achieve this goal, a combination of materials, procedures and methods are applied. This chapter is allocated to specifying the materials and describing those procedures. The equipment used for this study is specified and the required figures and tables are shown in this chapter.

Section 3.2 specifies the material used for this research. The common materials such as 70% nitric acid and distilled water do not appear in this part. Section 3.3 presents the procedures, the methods and the equipment used during the research.

3.2 Materials

3.2.1 Ore

The ore is obtained from a copper mine in the Gaspe region, Quebec. The ore rocks are crushed into smaller particles but remain larger than 25.4 mm (1 inch) in nominal diameter.

3.2.2 Rhamnolipid (JBR215)

The biosurfactants used are rhamnolipids with the trademark JBR215 from "JENEIL BIOSURFACTANT CO., LLC". JBR215 is an aqueous solution of rhamnolipid at 15% concentration. It is produced from sterilized and centrifuged fermentation broth. Two major types of rhamnolipids, RLL (R1) and RRLL (R2), are present in the solution.

The molecular weight of RLL ($C_{26}H_{48}O_9$. rhamnolipid type I) is 504 and of RRLL ($C_{32}H_{58}O_{13}$, rhamnolipid type II) is 650 as determined by the supplier. The chemical structures of both types are given in Chapter 2 (Fig. 2-2).

Several tests done by the manufacturer and independent laboratories show the degree of biodegradability and toxicity of JBR215 match the EPA requirements.

Some physical and chemical properties of these types of JBR215 are shown in the Table 3.1.

Table 3-1 Physical and chemical properties of JBR215 (adapted from Jeneil Biosurfactant Co. Ltd. 2001)

Physical/ Chemical property	Description
Appearance	Dark brown
Concentrations	Viscous suspension
Odor	Mild cooked odor
Specific Gravity	1.12 – 1.14
PH	6.5 – 7.5
Solubility in water	Soluble at neutral pH
Suitable diluents	Water and most common alcohols
Suggested starting	Active rhamnolipid Ingredient: 0.01, 0.1, and 1.0%
Surface tension	29 mN/m
Interfacial tension	0.3 mN/m

The biosurfactant is supplied as a 15% concentration solution. According to previous studies (Mulligan 1998), the optimum concentration is 2% that is in the order of magnitude of one. Therefore, each 1mL of biosurfactant was diluted to 15mL with distilled water to obtain a solution of 1% concentration or to 7.5mL for a solution of 2% etc.

3.3 Procedure

In this study, a set of tests was designed to find the optimum values of the parameters involved in the extraction process. This section presents all the tests done in chronological order. The equipment used for each test is specified in the description of the test.

i. Ore preparation and ore digestion

Ore preparation including grinding, colloid removal by water washing, sieving and ore digestion as the first step on this experimental approach. The ore was crushed and sieved to find the best size for the ore particles in the extraction process. The maximum sieve size chosen was number 5 and the minimum was number 200. All particles remaining between those two sieves were used for the size optimization test. To remove colloidal materials from the particles, the ore was washed with water. Using method ASTM D422 (ASTM 1970), the washed materials were placed in an oven and dried at 100°C for 24 hours. The next step is sieving in which a series of sieves were arranged in a column from bigger to smaller mesh. The ore was poured to the top sieve (sieve number 5) and then the column was shaken for 15 minutes. Since the grinding had no standard, the size distribution diagram was not drawn.

The ores collected from the sieves were kept separately in a dry keeper (Model Sanplotec).

The prepared ore was digested. The method recommended by Environment Canada (1990), for digestion of ores containing copper, was used to digest the ore. The following method includes nine steps and an average of four tests was accepted as the result.

i. 1.00 g of the ore was placed in a 1L beaker.

ii. 100mL of 16N nitric acid was added to the beaker over a minimum period of 2 minutes.

iii. 40mL of H_2O_2 (30%) was added to the beaker. The beaker was left for 5 minutes to react.

iv. The beaker was placed on a hot plate (Fisher Stirring Hotplate) until it boiled. Then, it was removed from the heat and cooled to room temperature.

v. A solution of 1000mL Aqua Regia was made through the following process:

   a. 200mL of concentrated nitric acid was added to a 1000mL flask.

   b. 500mL of distilled water was added to the flask.

   c. 50mL of concentrated hydrochloric acid was added to the flask.

    d. The flask was filled to 1000mL with distilled water.
vi. 200mL of Aqua Regia was added to the beaker.
vii. The beaker was filled to 500mL with distilled water.
viii. The solution was prepared for Atomic Absorption Spectrophotometer.
ix. The amount of copper was measured.
x. The process was repeated four times and the average was calculated.

ii. CMC measurement

There are several methods to determine the CMC for biosurfactants (Fig. 2-2). The CMC was found by graph conductivity, turbidity, surface tension, detergency and interfacial tension versus concentration (Myers 1992). In this test, using the variation of conductivity by change in the biosurfactant concentration, the CMC was determined. Conductivity was measured with a digital conductivity meter (Fisher Scientific).

iii. ***Copper extraction***

The percentage of copper extraction can be calculated through the following equations:

$$\text{mg copper}_{\substack{\text{in soluton}\\ \text{after washing}}} = \left(\frac{\text{mg}}{\text{L}}\frac{\text{copper}}{\text{biosurfactant}}\right) \text{x} \left(\frac{1\,\text{L}}{1000\,\text{mL}}\right) \text{x}\ 10\text{mL} \qquad [3\text{-}1]$$

$$\text{mg copper}_{\text{in ore(initial)}} = \left(\frac{\text{mg copper}}{\text{kg ore}}\right) \times \left(\frac{1\,\text{kg}}{1000\,\text{g}}\right) \times 1.00\text{g} \qquad [3\text{-}2]$$

$$\%\ \text{copper extraction} = \left(\frac{\text{mg copper in solution}}{\text{mg copper in ore}_{\text{(initial)}}}\right) \times 100\% \qquad [3\text{-}3]$$

iv. Optimization of the ore particle size

This test was to find the best size of ore particle to be used in the copper extraction process. Particle size not only affects the rate of extraction but also makes a difference in the cost of preparation. Bigger particles need less energy for crushing than do finer particles.

By sieving, ore particles are classified and shown in Table (3-2). A quantity of 1.00g from the ore of each particle size was placed in individual 50mL vials.

Table 3-2 Sieves and mesh opening sizes

Sample	Sieves No.	Mesh Opening Size(mm)
1	5 – 10	4 – 2
2	10 – 16	2 - 1.18
3	16 – 20	1.18 - 0.85
4	20 – 30	0.85 – 0.595
5	30 – 50	0.595 – 0.3
6	50 – 100	0.3 – 0.15
7	100 – 200	0.15 - 0.075

10.0mL of 1% concentration surfactant was added to each vial. In all vials the pH was set at 6.5 and the samples were kept in the temperature incubator at constant temperature (25°C) for 5 days. Blank samples including 10.0mL distilled water and 1.00g ore were provided for all sizes.

Vials were placed on the side in order to achieve the maximum contact surface between the ore particles and the biosurfactant. The solutions from each sample were collected. The samples were digested and the concentration of copper in each sample was measured by the Atomic Absorption Spectrophotometer (Perkin Elmer Aanalist 100). The maximum concentration defines the optimum particle size for extraction.

In order to release the copper trapped in the biosurfactant micelles by oxidizing the organic copper colloids were oxidized by adding 30% H_2O_2 slowly until no reaction was observed.

The method chosen for biosurfactant digestion was 3030E, which is recommended by APHA (1989) and approved by EPA. The steps of the method are:

i. 50 mL of the mixed sample was transferred to a 125 mL beaker.

ii. 25 mL of concentrated HNO_3 and a few boiling chips were added to the beaker's contents.

iii. The beaker was heated over a hot plate and brought to a slow boil.

iv. The digestion was considered done when the solution in the beaker became a clear light-colored liquid.

v. The solution was cooled to room temperature, filtered through filter paper (40 ashless circles, 110 mm diameter x 100 circles) and the volume returned to the initial volume (50 mL).

v. Effect of shaking

This test was designed to find whether shaking improves copper extraction. One gram of ore of optimum size was placed into six vials. Ten mL biosurfactant of 1% concentration at pH 6.5 was poured into each vial. All samples were placed on the shaker into the incubator where the temperature remained constant at 25°C. After 5 days the samples were taken out of the low temperature incubator and liquid collected. Using the biosurfactant digestion method, the concentrations of copper in the solutions were measured by the Atomic Absorption Spectrophotometer.

vi. Optimization of the pH

To investigate the effect of pH on the extraction process, this test was designed. Since copper precipitates at a pH less than 6, pH values of 6, 6.5, 7.5, 8.5, 9.5, and 10.5 were selected in this test.

For each pH, three samples were taken. One sample contains 1.0 g ore and 10.0 mL distilled water and the other two samples contain 1.0 g ore and 10.0 mL of the 1% concentration of biosurfactant each. The pH was adjusted by HNO_3 or NaOH. After 5 days in the constant temperature of 25°C without shaking, the solution was collected, digested and the copper concentration was measured. The pH of the sample with the maximum concentration of copper was considered as the best pH.

vii. Evaluation of the ore to the surfactant ratio

To find the best ore to biosurfactant ratio, 1.00 g of the optimized size of ore and 1% concentration biosurfactant with optimized pH were placed in the vials. The volumes of the solution in the vials were 2.5, 5, 10, 20, 30, 40 and 50 mL. The vials were kept at a constant temperature of 25°C for 5 days. Then the solutions were digested and using the Atomic Absorption Spectrophotometer the copper concentration of each sample was measured to find the best ore mass to biosurfactant volume ratio.

viii. Time study

Samples were taken for the optimum conditioned samples at 1, 2, 3, 4, 5, 6, 7, 8, 11, and 14 days. A detailed discussion on the results is presented in the next chapter.

ix. Effect of the concentration of the biosurfactant

A test was performed to determine the most efficient concentration of biosurfactant used in the extraction process. The selected concentrations in the test were 0.05, 0.1, 0.2, 0.4, 0.5, 1.0, 2.0, 4.0 and 5.0%. All samples contained 1.0 g of ore and all other parameters were optimized.

The solutions were digested and the copper concentration was determined for each sample.

x. Effectiveness of NaOH on the extracting process

The effect of NaOH on the extraction was also investigated. The idea of using NaOH to extract more copper in lower concentration of surfactant was raised through previous research (Mulligan 1998).

To compare the effectiveness of NaOH, the same concentrations of biosurfactant used in test (ix) were used in this test with the addition of 1% NaOH to each sample. The same procedure was followed to extract the copper and digest the solution and analyze the concentration of copper in the solutions.

xi. Effect of Several Washings on the process

In the multiple washing test, the optimized solution was added to a vial containing 1.0 g ore. After 24 hours, the solution was taken out and a new solution with the same volume and other conditions was used. This process was repeated six times (6 washes). The copper extracted was determined in each wash and then added to obtain the total.

xii. Unwashed ore sample test

The biosurfactant optimized solution was added to an unwashed ore sample under the optimized conditions. This test shows how the optimized conditions obtained from the previous tests of this research are valid for a real field crushed ore (Fig. 3-3). The only restrictions for the size of the ore particles were that they were allowed to pass through the sieve no. 5 and that the sample represented the whole crushed ore. In this test, 10.0 g of ore were placed in the vials with 100 mL of biosurfactant.

The test was done under two conditions: with shaking and without shaking. In the case of shaking, samples were locked to the shaker that operated at 100 rpm (Figs. 3-4 and 3-5). The shaker is a platform shaker brand Innova™ 2000.

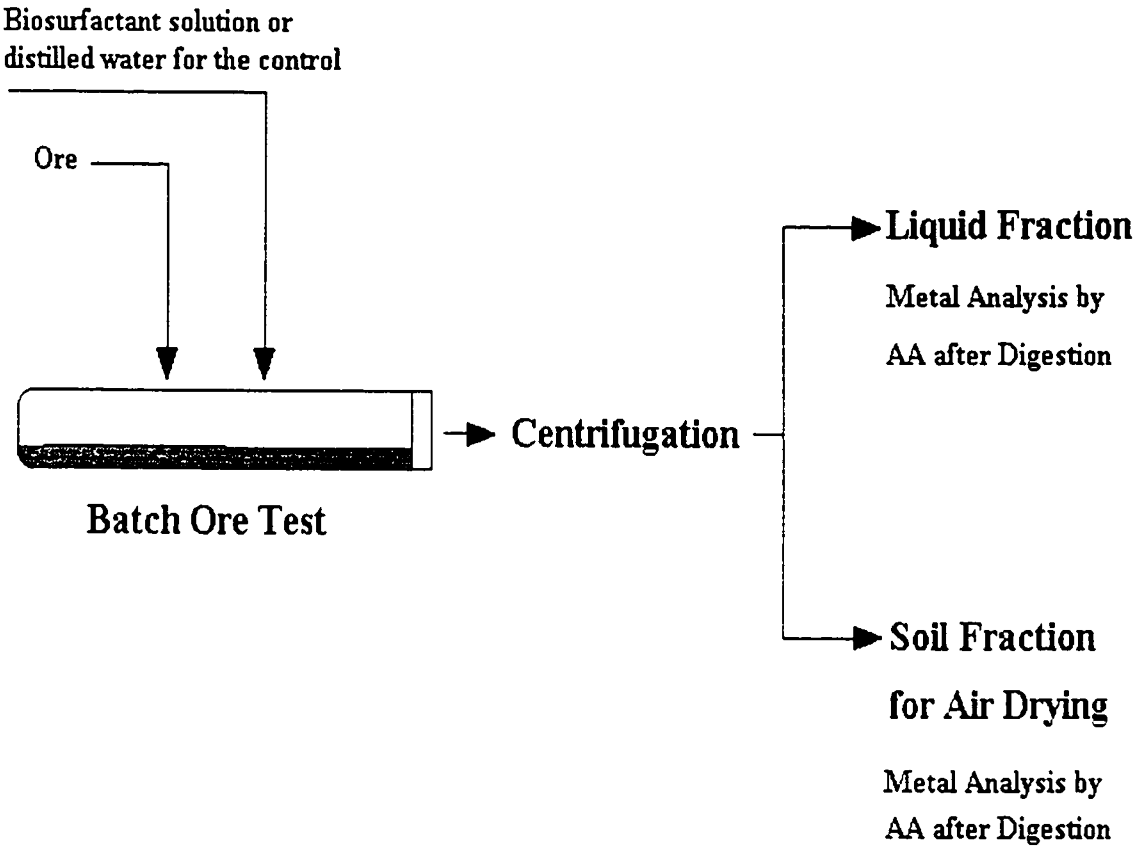


Figure 3-1 **Batch ore extraction procedure**

The last part of this test was to perform mass balances. In order to determine copper extraction, the concentration of copper in the ore was initially found (before the tests). After the tests, using equations [3-4] and [3-5], the concentrations of copper in both biosurfactant and the ore were determined.

$$\text{mg copper}_{\substack{\text{in biosurfactant}\\ \text{solution}}} = \left(\frac{\text{mg}}{\text{L}}\frac{\text{copper}}{\text{biosurfactant}}\right) \text{x} \left(\frac{1\,\text{L}}{1000\,\text{mL}}\right) \text{x}\ 100\,\text{mL} \qquad [3\text{-}4]$$

$$\text{mg copper}_{\text{in the ore after the extraction}} = \left(\frac{\text{mg}}{\text{kg}}\frac{\text{copper}}{\text{ore}_{\text{after extraction}}}\right) \text{x} \left(\frac{1\,\text{kg}}{1000\,\text{g}}\right) \text{x}\ 10.00\,\text{g} \qquad [3\text{-}5]$$

The equation used for mass balance is:

$$\begin{aligned}\text{mg copper in ore}_{\text{initial}} &= \text{mg copper}_{\text{in biosurfactant}} \\ &+ \text{mg copper}_{\text{in ore after the extraction}}\end{aligned} \qquad [3\text{-}6]$$

xiii. Sequential extraction

Sequential extraction of the copper ore includes several steps to determine the portion of each copper component in the ore. The following table (Table 3-3) shows the procedure. A sample of 1.5 g of dried ore was placed in 15mL of 2% rhamnolipid and another 1.5 g of dried ore was placed in 15mL of distilled water for 6 day to determine the soluble fraction.

Each of the fractions was taken and the concentration of copper was measured in each of the fractions by atomic absorption spectrometry. The amount of copper extracted from the ore in each fraction was then calculated.

Table 3-3 Sequential extraction process (Adapted from Mulligan 1998)

Order of sequence	Chemical reagents	Ore fraction
1	Extraction of copper by rhamnolipid and distilled water overnight with 15 mL of solution	Soluble
2	Extraction of copper with 8 mL of 1 M $MgCl_2$ (pH 7) for 1 hour	Exchangeable
3	Extraction of metals with 8 mL of 1 M sodium acetate NaOAc adjusted to pH 5 with acetic acid for 5 hours	Carbonates
4	Extraction of metals with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid pH 2.5) at 96°C for 6 hour	Oxides and hydroxides
5	Extraction with 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 (pH 2) for 2 hours at 85°C, followed by 3 mL of 30% H_2O_2 (pH 2) for 3 hours at 85°C and then 5 mL of 3.2 M ammonium acetate NH_4Oac in 20% (v/v) HNO_3 diluted to 20 mL at room temperature for 30 minutes	Organic matter
6	Digestion at 90°C with 25 mL of dilute aqua regia (50mL HCl, 200 mL HNO_3 and 750mL water) for 3 hours	Residual fraction

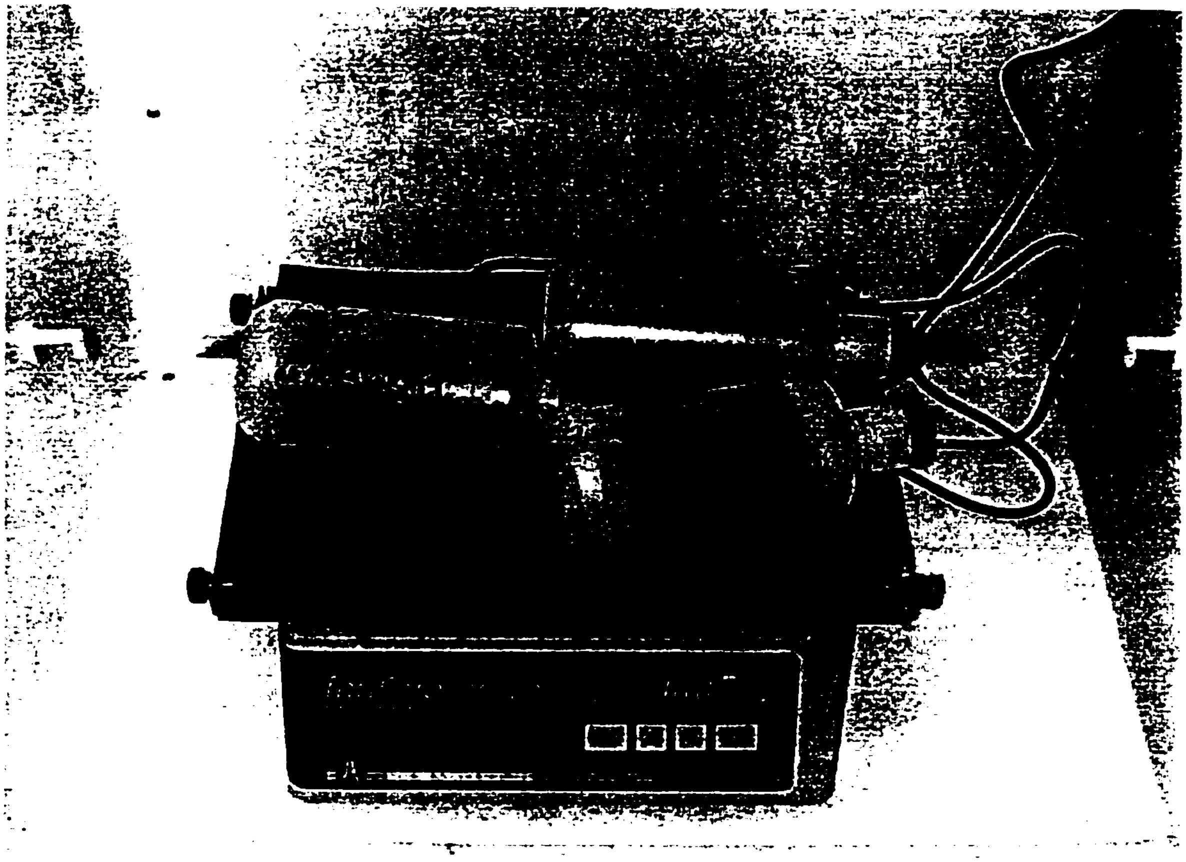


Figure 3-2 Samples of the test (xii) with shaking

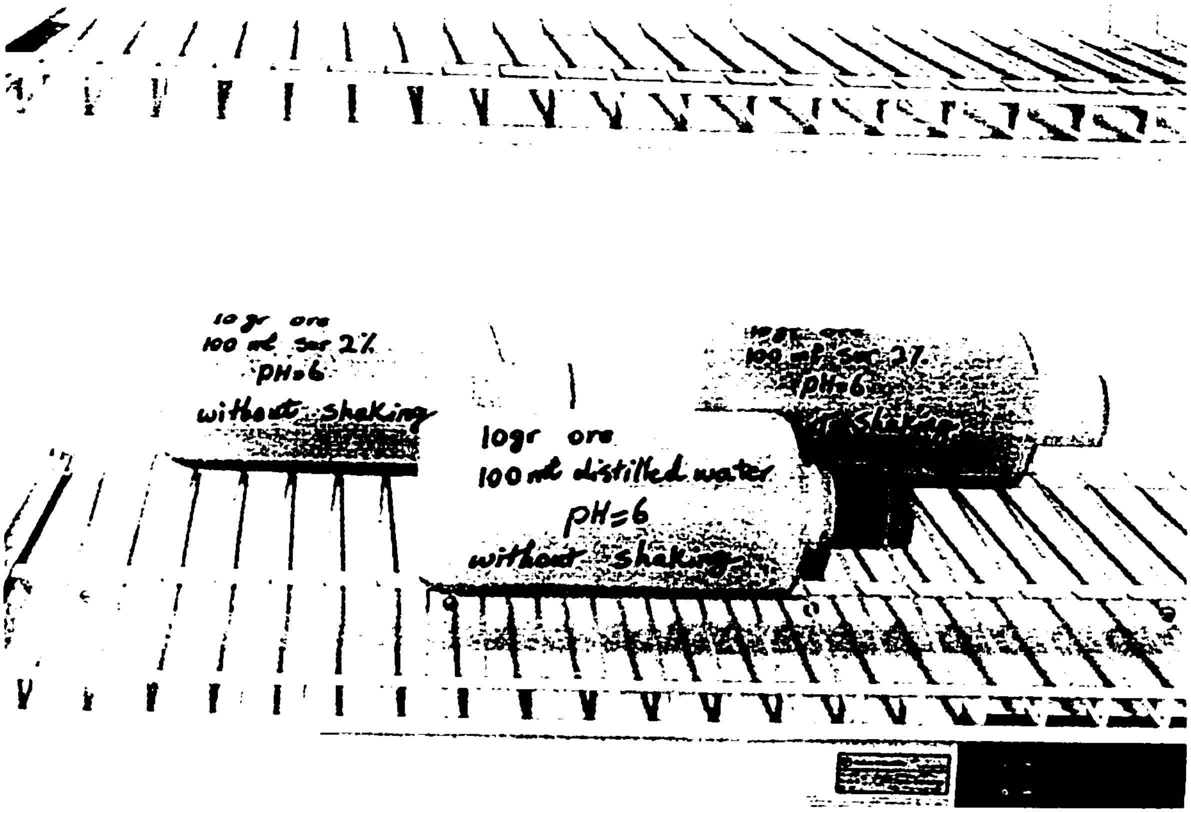


Figure 3-3 Samples of the test (xii) without shaking

Chapter 4

Results and preliminary discussions

4.1 General remarks and material characteristics

In this chapter, the results of the experiments are presented. As mentioned earlier in this thesis, several tests were designed and performed. For each test a preliminary discussion is presented. In each test, one condition was varied and the resulting extraction was found. Depending on the nature of the test, the optimum value was chosen. To find the proper range for the variation of the parameters studied, those from related literature were used.

The extraction percentage given in the charts is the ratio of the mass of extracted copper that measured in the solution to the initial mass of copper in the unprocessed ore in percent. The average values of two samples were used for each result. The result of each test was supported with the next test and difference of two samples in each test is limited to10% (5%-10%).

4.1.1 Ore characterization

The copper in the ore was measured by an Atomic Absorption Spectrophotometer. An ore digestion test was designed and completed. The following equation [Eq. 4-1] is used to calculate the mass of copper in 1kg of ore and results are shown in the following table (Table 4-1).

$$\mathrm{Cu}_{\text{in digested ore}}\left(\frac{\text{mg}}{\text{L}}\right)\times\frac{1\text{L}}{1000\text{ mL}}\times\frac{500\text{ mL}}{1.00\text{ g ore}}\times\frac{1000\text{ g}}{1\text{kg}}=\frac{\text{mg copper}}{\text{kg ore}} \qquad [4\text{-}1]$$

Table 4-1 The results of ore digestion

ore digestion(mg/L)	mg Copper/kg Ore
17.7	8850
17.6	8800
17.2	8600
17.1	8550
18.1	9050
18.2	9100
19.1	9550
18.2	9100
Average = 17.9	Average = 8950 Variance=323

This measurement led to the mass of copper in the ore. According to this measurement, in 1kg of ore 8950 mg copper exists and, therefore, this ore is graded as “Low Grade”.

4.1.2 Rhamnolipid CMC

Most of the rhamnolipid properties are given in Chapter 3. In this section, the measurement of CMC is presented.

The crossing point of the two tangents of the curve is the CMC. As seen in Fig. 4-1, the value of CMC is about 0.035 g/L. This value is equivalent to 0.003% rhamnolipid. Therefore, in the rest of the experiments, a concentration above the CMC was used to ensure the formation of micelles.

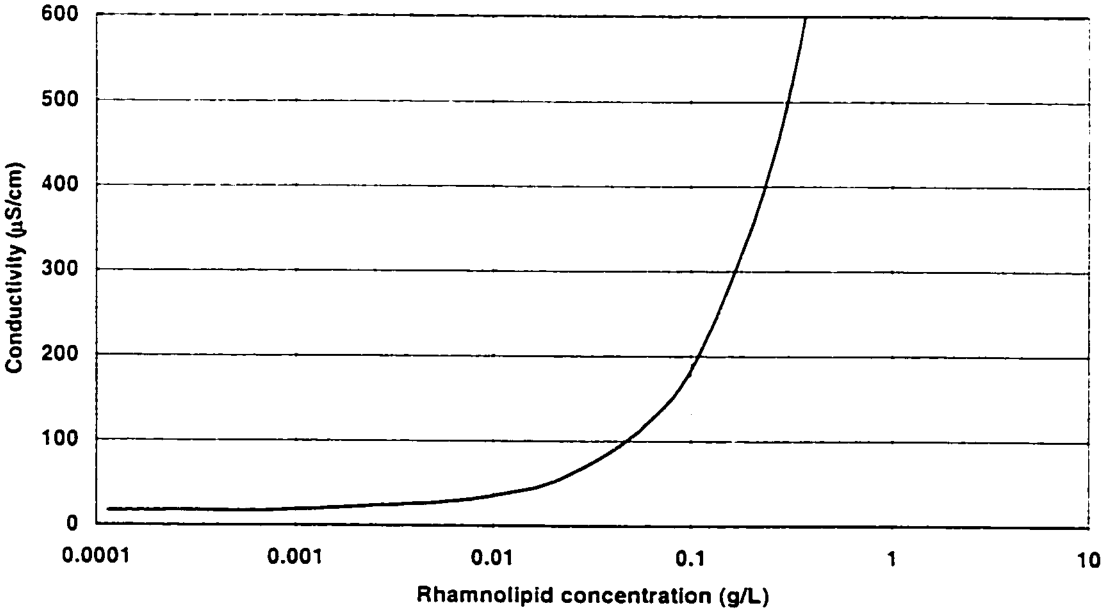


Figure 4-1 Conductivity versus concentration of rhamnolipid to find CMC

4.2 Results of tests

4.2.1 Effect of particle size

The ore particles were initially larger than 25.4 mm. Since this size was very large for use in the laboratory, the particles were crushed to smaller particles. Crushing is a common step in both pyrometallurgy and hydrometallurgy. The crushed particles were collected from those that passed through sieve No. 5 (opening size = 4 mm) but did not pass through sieve No. 200 (opening size = 0.075 mm). Seven ore samples were collected and one g of each was placed in each vial and 10 mL of the rhamnolipid solution of 1% (pH 6.5) was added.

Figure 4-2 presents the results of this test. The control is the same ore but in distilled water. The results show in the samples containing ore particles that passed sieve No. 50 (0.3 mm) and left on sieve No. 100 (0.15 mm), the maximum copper extraction was 17.7%.

The extraction of copper from ore depends on the contact surface area between ore and the solution. The following shows how the contact surface area changes for various sizes of particles.

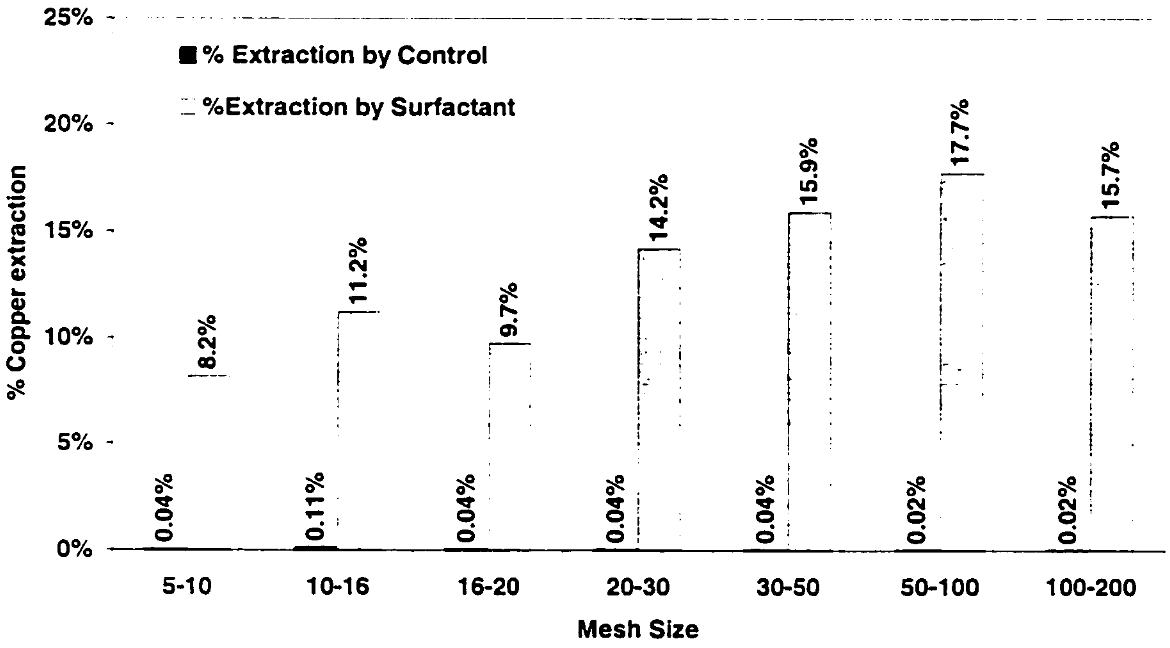


Figure 4-2 Extraction of copper from ore with various particle sizes

The calculation is done for spherical particles that have the minimum surface area for a constant volume. Since we assume that the ore is homogeneous and that the ore density is constant, therefore, two equal masses of ore have the same volume.

$$\text{Volume} = n\alpha a^3 \qquad [4\text{-}2]$$

$$\text{Area} = n\beta a^2 \qquad [4\text{-}3]$$

$$\frac{\frac{V_1}{A_1}}{\frac{V_2}{A_2}} = \frac{\frac{n_1\alpha a_1^3}{n_1\beta a_1^2}}{\frac{n_2\alpha a_2^3}{n_2\beta a_2^2}}$$

Since V_1 is chosen to be equal to V_2 therefore:

$$\frac{A_2}{A_1} = \frac{a_1^2}{a_2^2} \qquad [4\text{-}4]$$

Where “a” is the diameter of the particle. It means the volume containing the smaller particles has more surface area and more surface area gives more extraction. The improved extraction in finer ore particles is a result of bigger contact surface between them and the biosurfactant.

Another parameter is the part of the surface that is in contact with the other particles. Since for particles smaller than 0.15 mm in nominal diameter, this area is more than that for the bigger particle, the extraction will be small for very fine particles. There is a maximum contact surface in particles with diameter between 0.3 mm and 0.15 mm that was found in this study.

4.2.2 Effect of shaking

A test was designed to find whether shaking affects the extraction. In this test one gram of ore with the same size as used in the previous test was placed in 10 mL of the 1% rhamnolipid (pH 6.5) and the vials were fixed on a shaker. The shaker was set at 100 rpm and after 5 days, the solutions were digested and the extractions were measured. The extraction with distilled water was used as the control.

The results are shown in Figure 4-3. Although the extraction of copper by rhamnolipid did not show a remarkable change in the average extracted copper (13.3% in the unshaken samples compare with 12.3% in the shaken samples), but apparently the shaking was more effective on the control than on the surfactant.

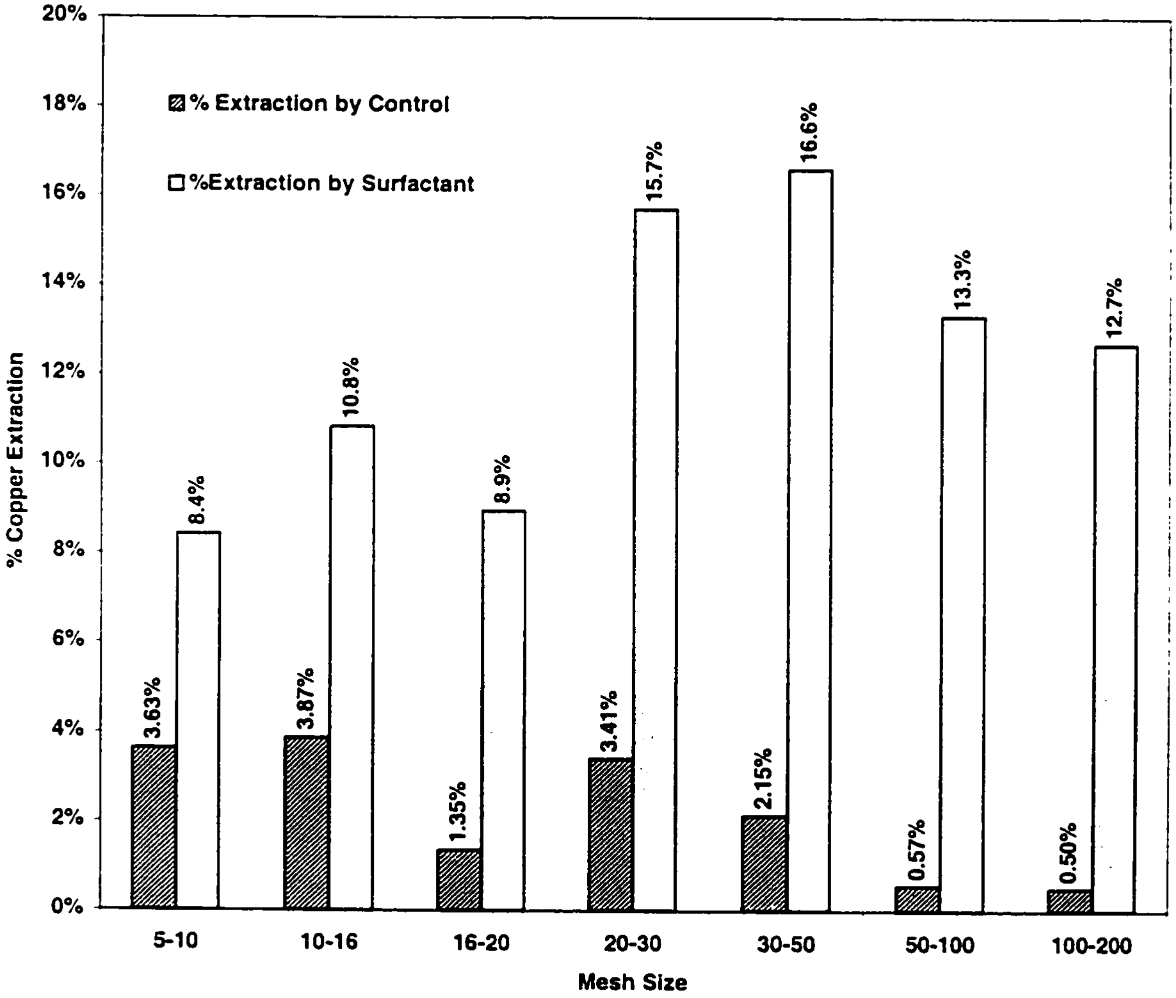


Figure 4-3 The effect of shaking

A comparative diagram in Figure 4-4 is presented. All controls were neglected since they were not significant.

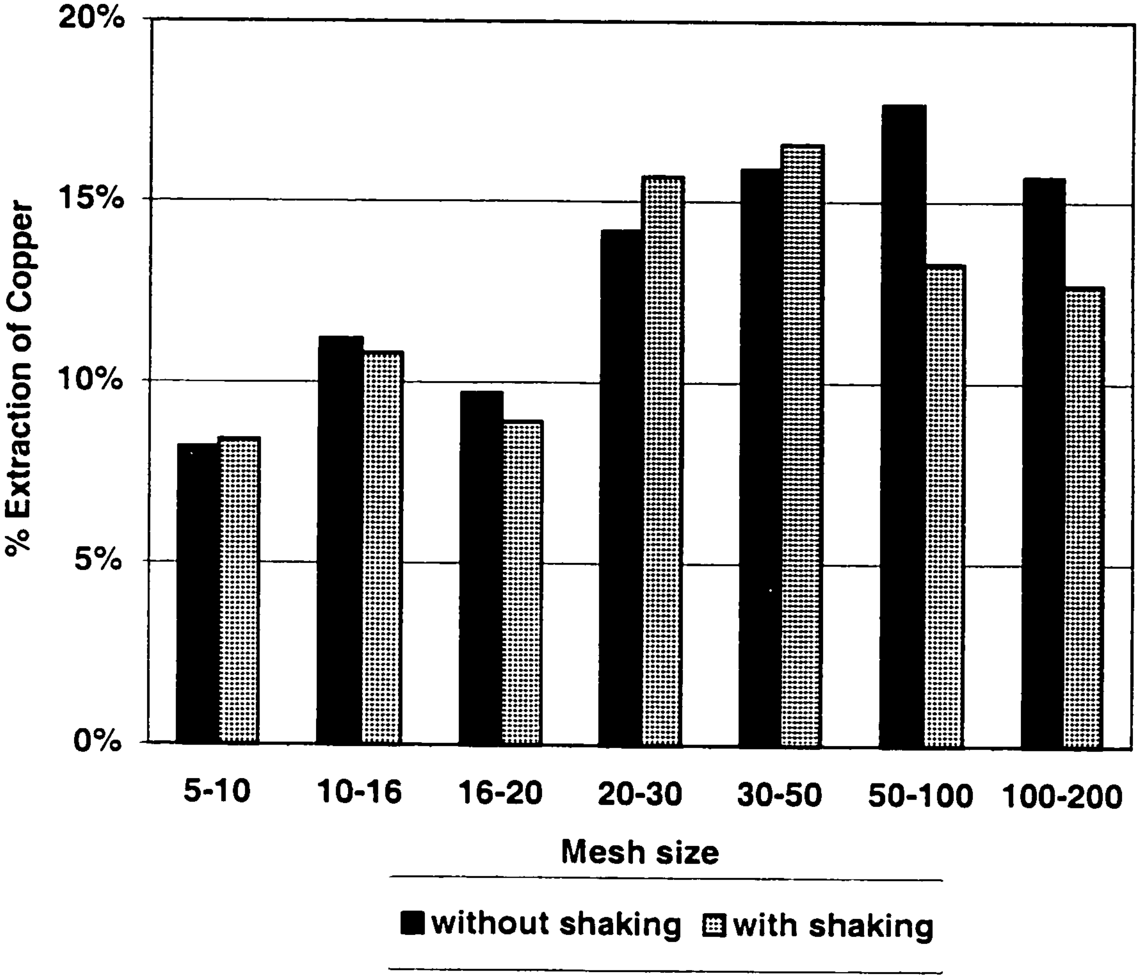


Figure 4-4 **Comparative diagram of copper extraction for the chosen particle sizes for shaken and unshaken samples.**

For the rest of experiment, the particles between sieve sizes No. 50 and 100 were used. Since the shaking did not improve the extraction and to avoid any new parameters in the experiment, the experiments were continued without shaking.

4.2.3 Effect of pH on copper extraction

Using the data from the first test, one gram of ore with particle sizes between 0.3 mm and 0.15 mm was placed in the vials with 10 mL of 1% rhamnolipid for 5 days at various pH values. The pH was adjusted to 6.0, 6.5, 7.5, 8.5, and 9.5 and the extraction efficiencies were found by the measurement of the copper concentration in the solutions. Figure 4-5 shows how the variation of pH affects extraction of copper from ore.

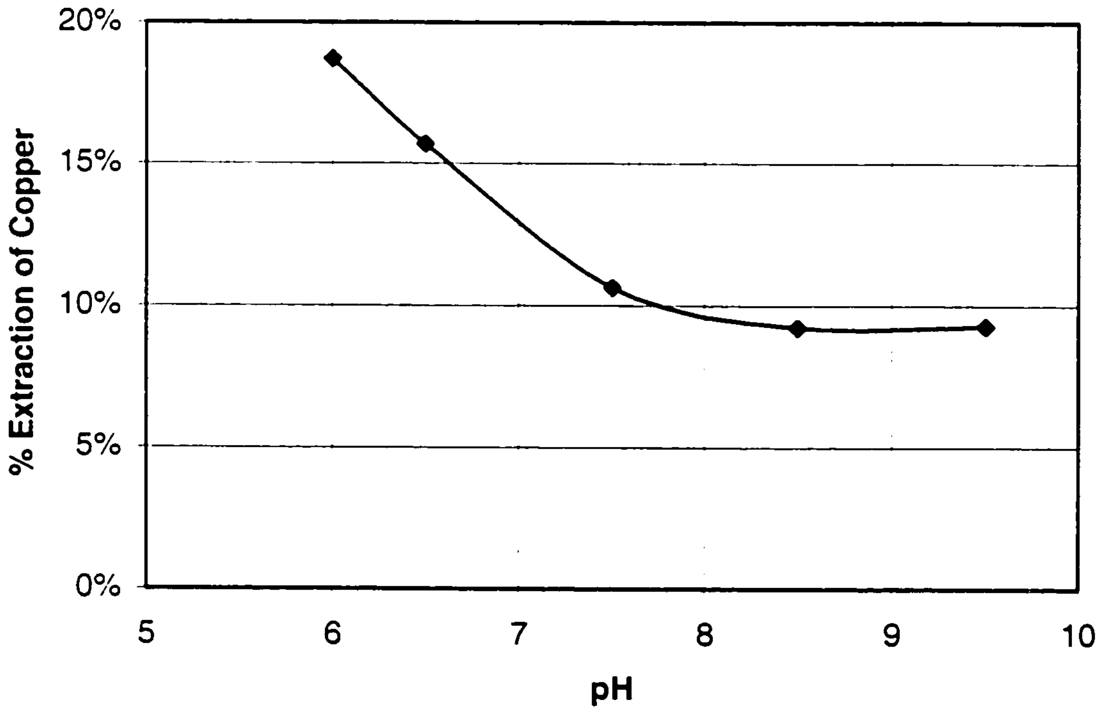


Figure 4-5 Variation of copper extraction with pH

The minimum extraction of copper occurred when the pH was around 8.8. According to Figure 4-6, the pH in which minimum solubility occurs is 8.7. It is similar to the result of this research and explain why at this pH (8.8) the extraction is minimal. When the pH is less than 5, the rhamnolipid precipitates and test cannot be completed. Since at pH =6 there was maximum extraction, this pH was chosen for the rest of the experiment.

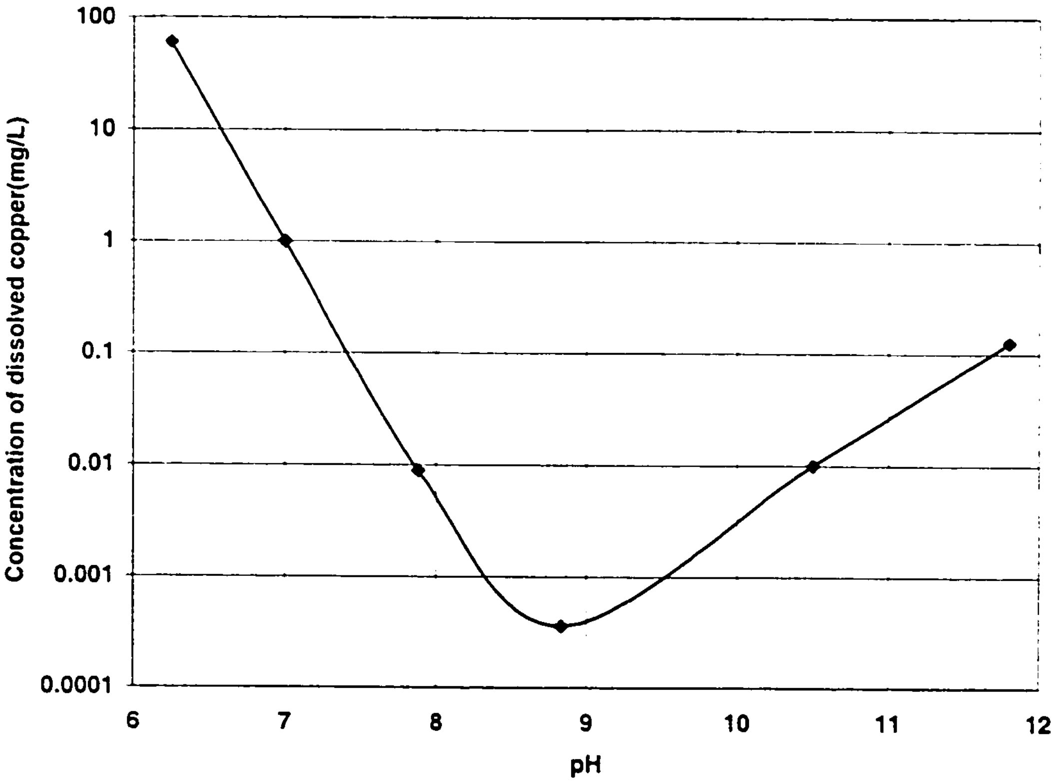


Figure 4-6 Solubility of copper hydroxides versus pH (Adapted from Radha Krishnan 1993)

4.2.4 Optimization of surfactant to ore ratio

In this test, one gram of ore was placed in 1% rhamnolipid with various volumes. The rhamnolipid volumes chosen were 2.5, 5, 10, 20, 30, 40, and 50 mL. The extracted copper was measured and the total mass of the copper was calculated. The ratio of the extracted copper to initial copper in the ore versus the volume of the biosurfactant, rhamnolipid, is presented in Figure 4-7.

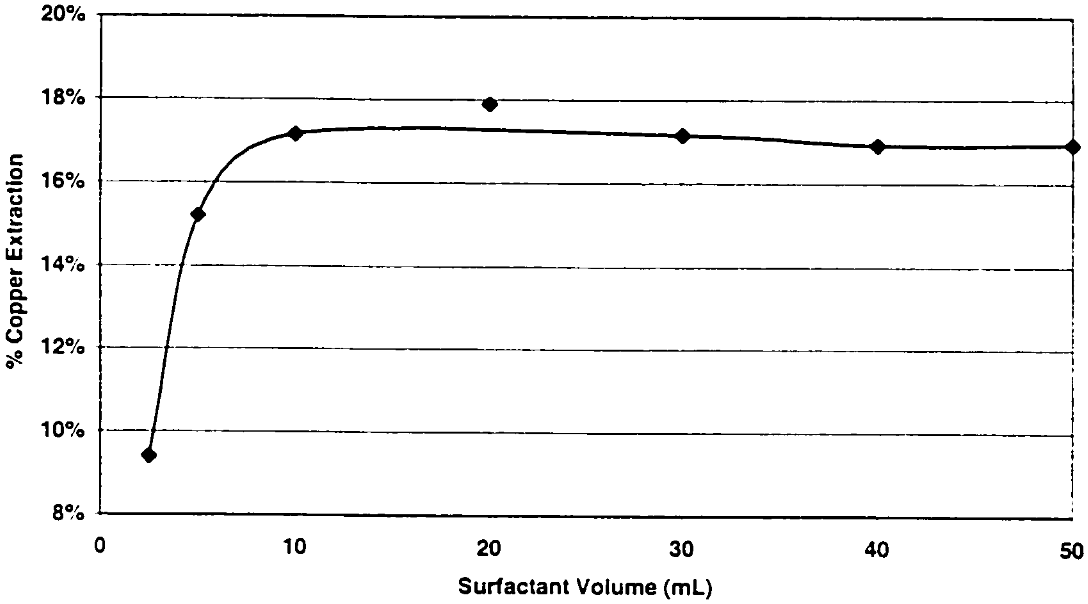


Figure 4-7 Variation of copper extraction with surfactant volume

The curve shows that increasing the volume increases the extraction for the first three volumes but when the volume exceeds 10 mL, this progress stopped and the curve flattens. The extraction (17%) is also very close to the existing data from previous tests.

It should be noted that this curve is as expected since the maximum possible extraction can not exceed a certain value. Volumes bigger than that volume can not improve the extraction.

It is also important to mention that the concentration of copper in the rhamnolipid is higher when the volume is smaller (332 mg/L in 2.5 mL biosurfactant comparing to 30.3 mg/L in 50 mL of the surfactant). The phenomenon looks very similar to saturation. The curve has a maximum at 20 mL but this could be due to experimental error. Therefore, 10 mL for 1.0 g ore is chosen to use in the experiment.

4.2.5 Time optimization

A test was designed to find the time at which the major portion of copper is extracted. In this experiment 1.0 g ore was placed in 10 mL biosurfactant, 1% rhamnolipid, and the extraction of copper was measured during a 14-day period.

The results of the measurement of extracted copper in the solution after 1, 2, 3, 4, 5, 6, 7, 8, 11, and 14 days are shown in figure 4-8. The extracted copper is compared with the initial copper in the ore. Several curves were tried and finally a logarithmic curve was fitted to these data with the equation given in the same figure.

As seen in the Figure 4-8 the extraction did not stop at 14 days. The curve does not show any local maximum and its maximum at day 14 apparently can not be counted as the maximum. To find an optimum time to be used in further tests, one can find a time at which the slope of the curve becomes less than 1% extraction per day.

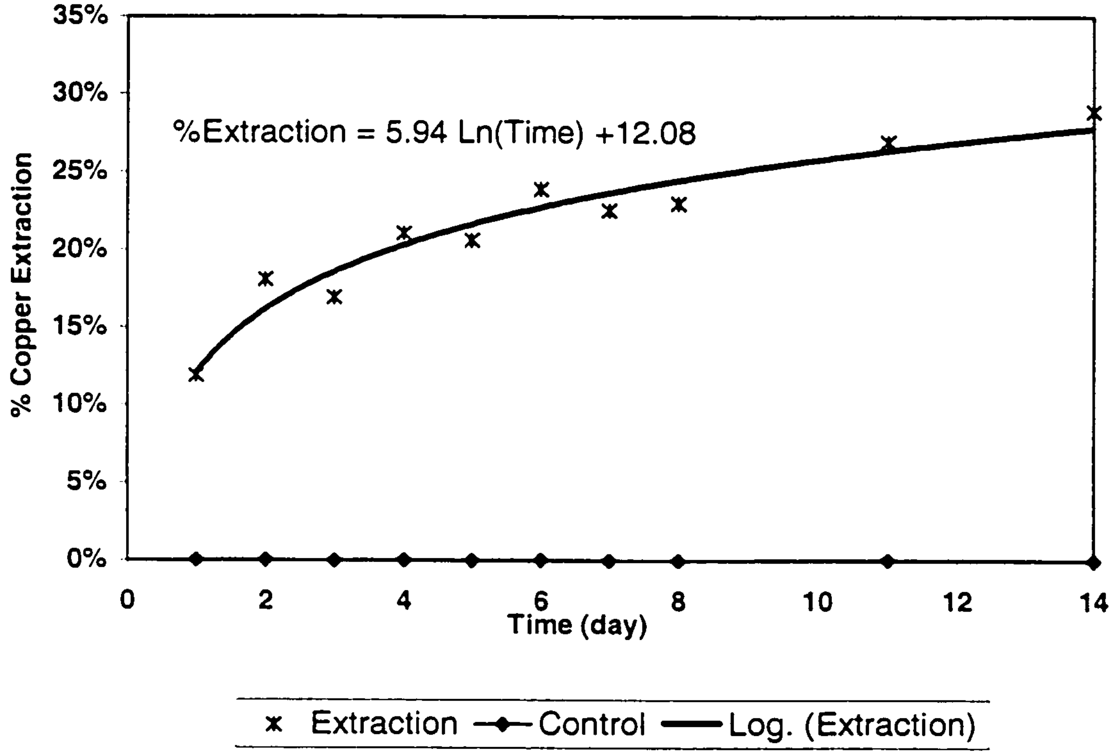


Figure 4-8 Progressive extraction of copper from ore by time

$$\text{Slope} = y' = \frac{5.94}{\text{Time}} = 1\%\ \text{extraction/day} \qquad [4\text{-}5]$$

Time = 5.94 ~ 6 days

And always:

$$y'' = \frac{-5.94}{\text{Time}^2} < 0 \qquad [4\text{-}6]$$

Which means the slope of the curve always decreases.

If 6 days is chosen as the optimized time, the difference with extraction from the next day will be:

$$\Delta y = \frac{23.64 - 22.72}{22.72} \times 100 = 4\%$$

This is fairly negligible.

Therefore, for the rest of the experiment, the pH was adjusted to 6, the particle sizes were between 0.15 and 0.3 mm, the weight of ore was 1.0 g in 10 mL of 1% rhamnolipid and it was extracted for 6 days.

4.2.6 Effect of the concentration of biosurfactant and NaOH

The test was designed to find the effect of concentration of rhamnolipid on copper extraction. Starting with 0.05%, concentrations of 0.1%, 0.2%, 0.4%, 0.5%, 1%, 2%, 4%, and 5% of rhamnolipid were prepared to extract copper from 1.0 g ore. The available rhamnolipid allows testing more concentrated solutions but if the concentration exceeds 5%, it will be considerably viscous and hard to work with.

Figure 4-9 shows the results of this test. As expected, higher concentrations extracted more copper (53.4% extraction with 5% rhamnolipid). The control with distilled water extracts 0.02% of copper while a very low concentration of rhamnolipid (0.05%) extracts 5.7% or 285 times more than distilled water.

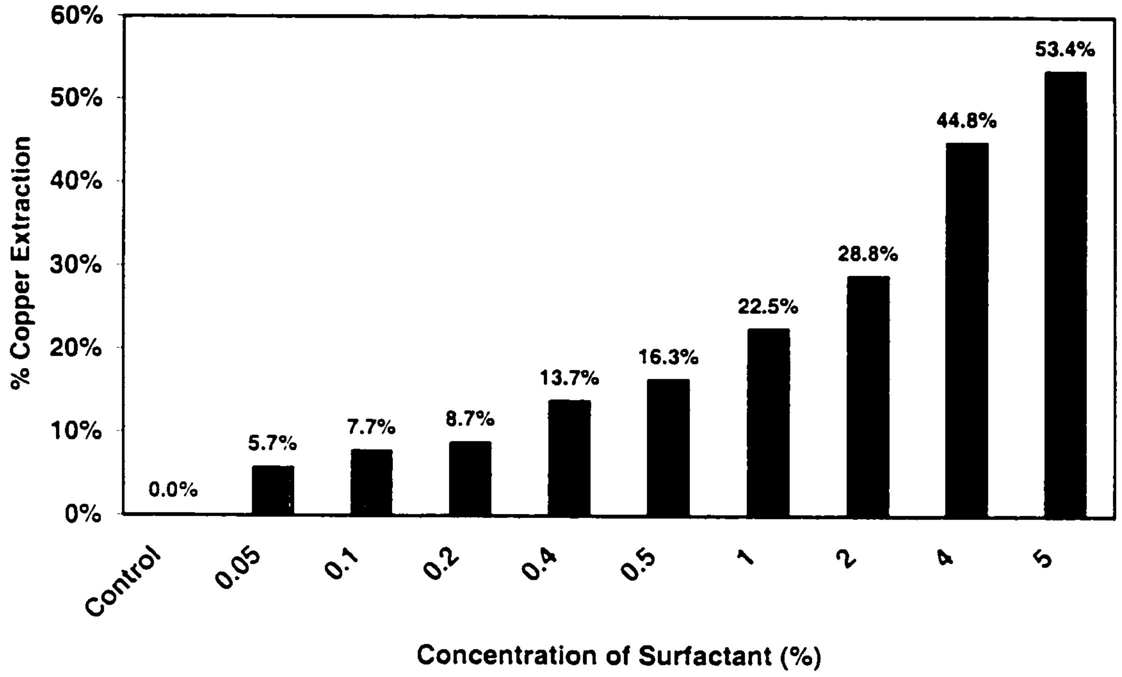


Figure 4-9 Extraction of copper at various concentrations of rhamnolipid

According to previous studies (Mulligan 1998), adding 1% NaOH to the solution will improve the copper extraction process. To verify the effect of NaOH, another test was designed in which the same concentrations are used but with 1% NaOH. The results are presented in Figure 4-10.

The figure shows a remarkable improvement in the extraction especially for 2% rhamnolipid (42.9%) which is higher than the 2% rhamnolipid with no NaOH in the last test (28.8%).

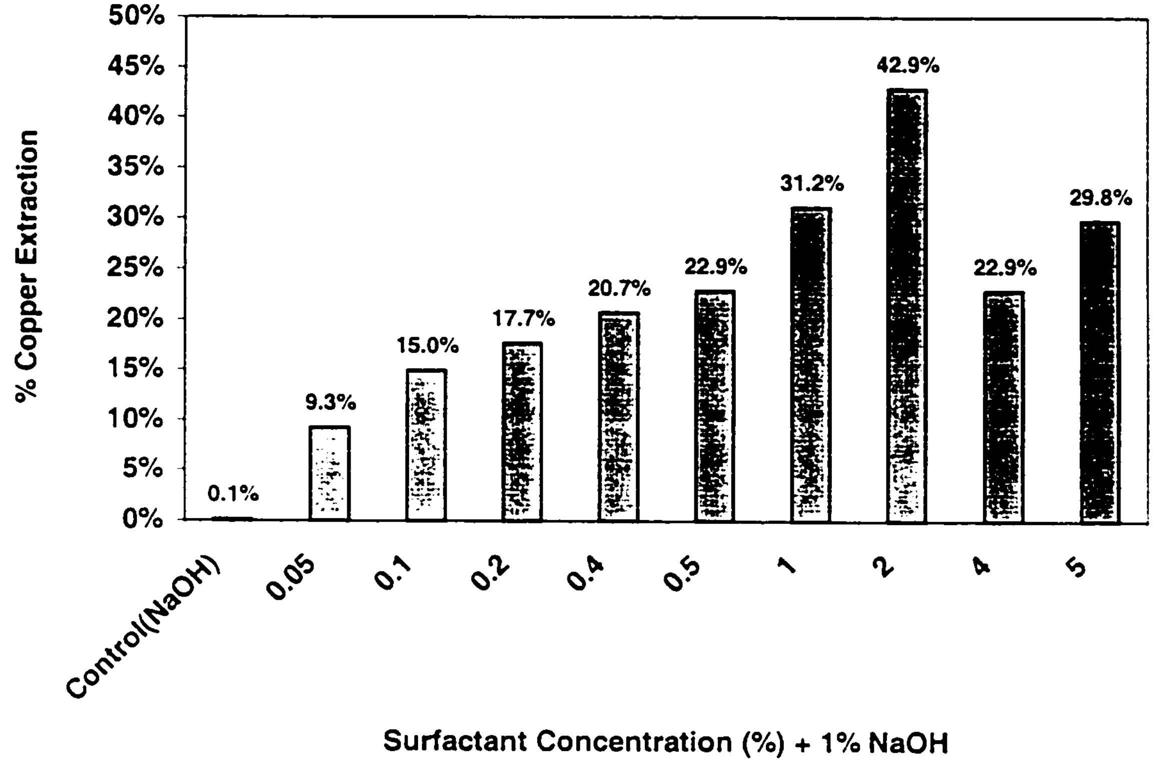


Figure 4-10 Copper extraction under the effect of various concentrations of rhamnolipid and 1% NaOH

To compare the results of these two tests, another graph is given in Figure 4-11. In this figure, controls are not shown since the controls do not have a significant extraction.

As the figure shows, the effect of NaOH is quite remarkable on copper extraction for concentrations of 2% rhamnolipid or less while it has a negative effect on the extraction for more concentrated rhamnolipid. In the later case the extraction of copper in the solution of 1% NaOH and 2% rhamnolipid has almost the same value as of 4% rhamnolipid without NaOH. The added NaOH increases the pH up to 13.5.

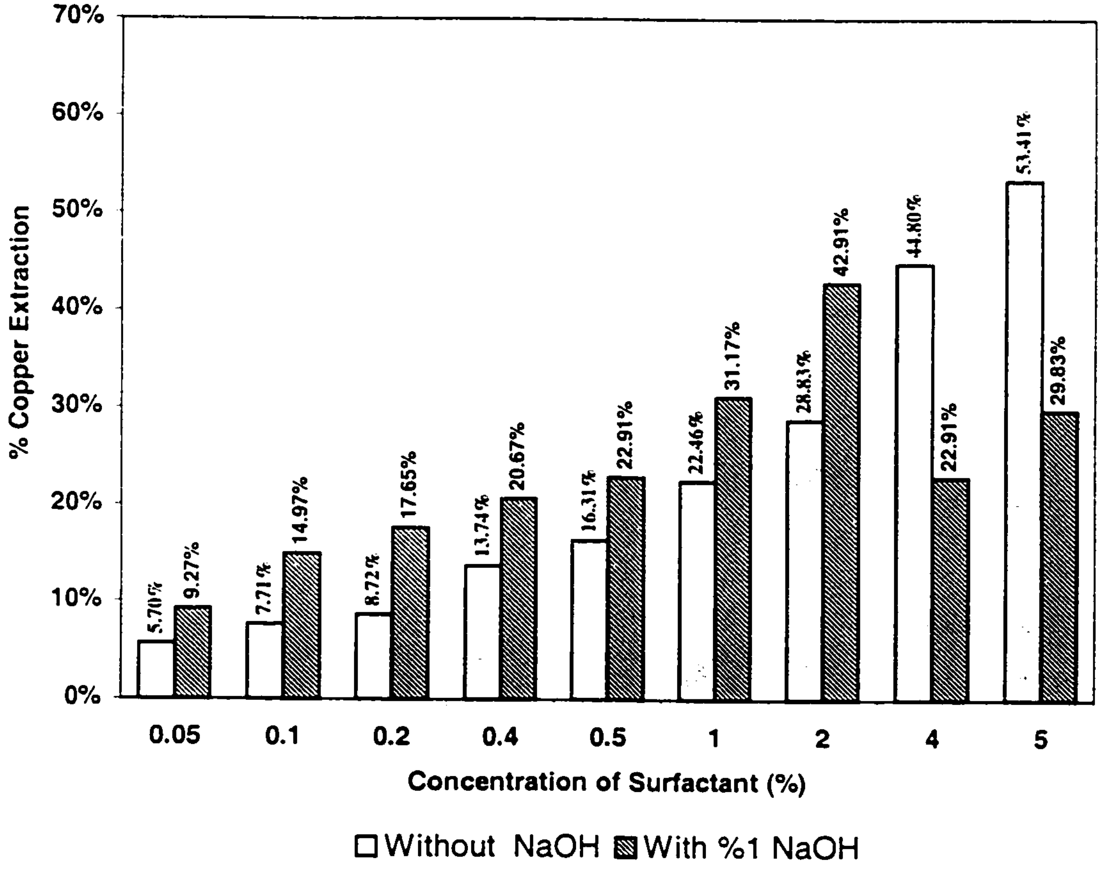


Figure 4-11 The effect of 1% NaOH on the extraction process for various concentration of rhamnolipid

4.2.7 Effect of multiple washes

The purpose of this test was to find the extraction of copper when the ore is in contact with fresh biosurfactant. This prevents saturation of the copper in the solution on the extraction process.

A 2% rhamnolipid solution was placed in the vial containing ore and after 24 hours was replaced with a fresh solution. Figure 4-12 shows an accumulative diagram of this serial washing during a 6-day test.

The existing data show the extraction of copper with a single wash is around 29% but with six times washing it becomes 32.2% which shows a relative 10% improvement (4% in total) in the copper extraction.

According to the previous tests in this research (section 4.2.4), the volume of biosurfactant did not affect the extraction as long as the minimum ratio of 10 mL rhamnolipid for 1.0 g ore is used. Therefore, the volume of rhamnolipid is not the influential parameter in several washings but the freshness of it plays a role in this increment.

To determine how these washings improve the total extraction, a diagram is used (Fig 4-13). The upper curve, curve A, shows the best fit curve for total extraction after each washing, similar to Figure 4-12 where the lower curve, curve B, is a best fit curve for the extraction due to each washing.

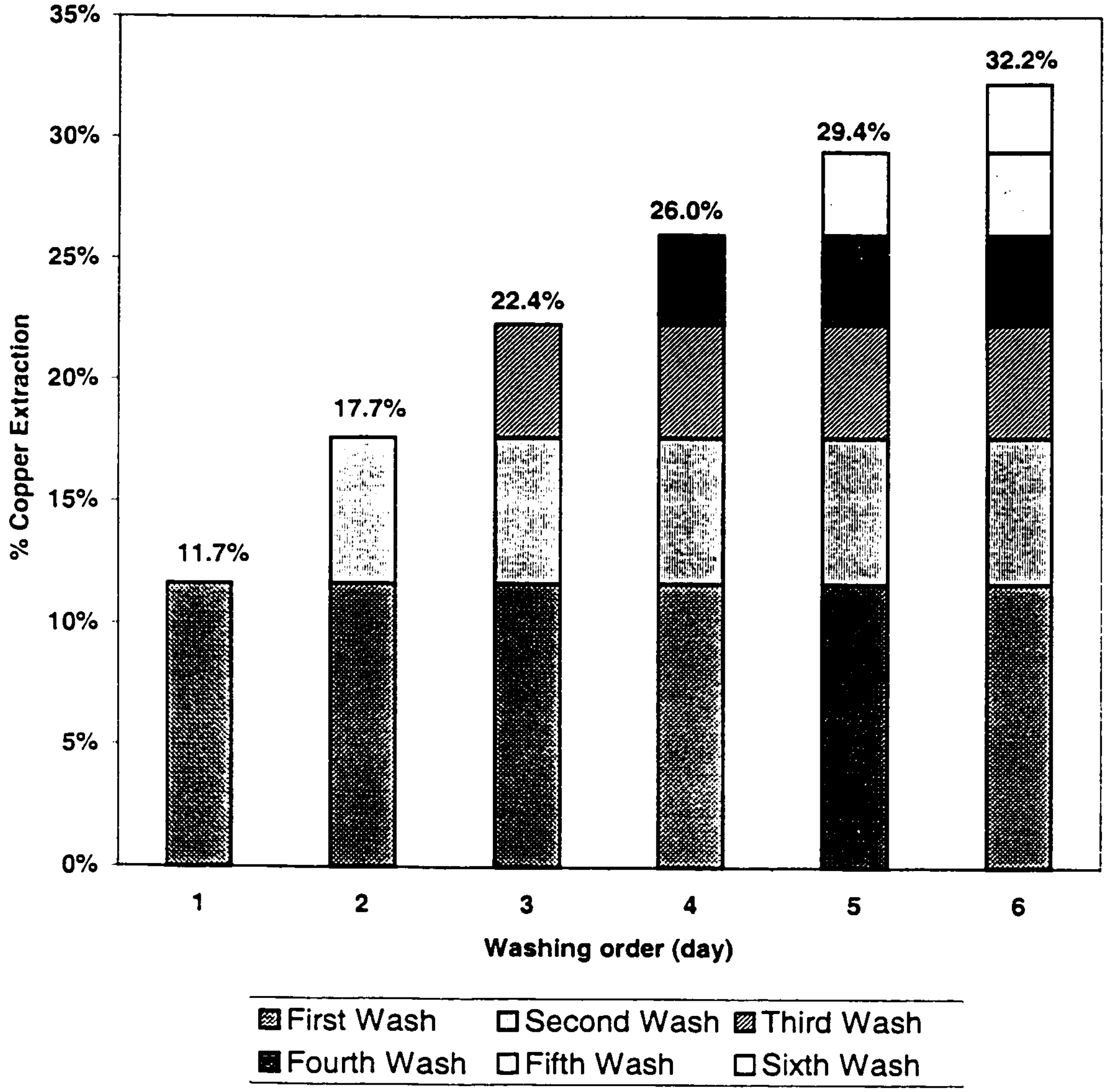


Figure 4-12 Accumulated extracted copper after a series of six washes of ore with 2% rhamnolipid

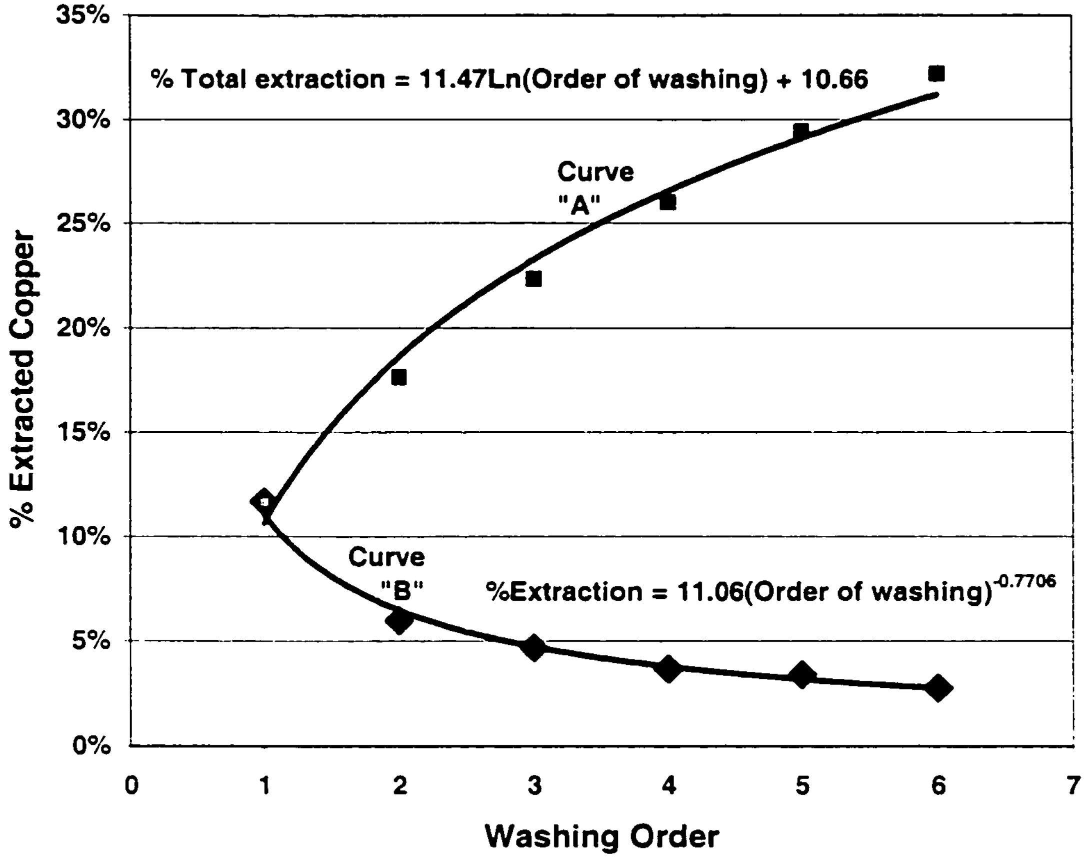


Figure 4-13 Accumulated extracted copper after a series of six washings of ore with 2% rhamnolipid (curve A) and extracted copper after each washing (curve B)

Those curves are the mathematical representations of the phenomena but they are not necessarily able to predict the extraction in a long term since both show the reaction takes a long time to remove all copper from the ore.

4.2.8 Extraction of copper from an unwashed ore sample

In this test, to simulate more closely the field samples a random combination of the ore particles was collected. All particles were passed through sieve 5 (opening size = 4 mm) and retained by sieve 200 (opening size = 0.075 mm). After taking the sample, the rest of the ore was sieved and the mass distribution over the sieves is shown in Table 4-2.

Table 4-2 Size distribution of ore particles used in the test

Mesh Size	g ore remaining on the Sieve	% ore remaining on the Sieve (Adjusted to total of 100%)
5 - 10	138.1	28.6
10 - 16	88.2	18.2
16 - 20	41.1	8.5
20 - 30	45.3	9.4
30 - 50	52	10.7
50 - 100	51.8	10.7
100 - 200	52.1	10.8
< 200	15.1	3.1
Total	483.7	100.0

The next step was to test the sample under both shaking and no shaking conditions when all other parameters such as particle sizes, pH, surfactant to ore ratio, time, and rhamnolipid concentration were optimized with the results of this study.

Four samples were prepared and after 6 days, both solution and the residue were digested in order to find the extraction and also to perform mass balances on the copper. The data are shown in the following tables. Table 4-3 shows the copper extraction in the solution and those for the ore. The control was distilled water.

Table 4-3 Results of digestion of solutions and residue for unwashed samples

	Sample in Surfactant		Sample in Control	
	Copper extracted to the Solution	Copper remaining in Ore	Copper extracted to the Solution	Copper remaining in Ore
With shaking	2143.5 mg	5550 mg	69 mg	7500 mg
Without Shaking	1792.5 mg	6200 mg	18 mg	8425 mg
%Copper in samples with Shaking	24.0 %	76.1 %	0.8 %	99.2 %
%Copper in samples without Shaking	20.0 %	80 %	0.2 %	99.8 %

The extraction of copper in an unwashed unshaken sample after optimization of time, pH, mass to volume ratio and rhamnolipid concentration becomes 20% while the shaken sample shows 24% extraction. The mass balance can be investigated through the summation of the total copper mass using equation [4-7].

$$\text{mass}_{\text{Cu in ore}} = \text{mass}_{\text{Cu in solution}} + \text{mass}_{\text{Cu in residue}} \quad [4\text{-}7]$$

Table 4-4 presents the mass balance in this test.

Table 4-4 Mass balance for unwashed samples

	Sample in Surfactant		Sample in Control	
	Total mass of copper in 1kg ore (mg)	Difference (%)	Total mass of copper in 1kg ore (mg)	Difference (%)
With shaking	7693.5	14.0	7569	15.4
Without Shaking	7992.5	10.7	8443	5.7

In the above table the difference was computed by dividing the difference between the total mass of copper in one kg of ore from this test and from the ore digestion, (8950 mg copper / one kg of ore) to the latter one.

The later test, unwashed samples in the optimized condition, showed that the size of particles is a very important parameter in the extraction process. Under the same conditions, samples of ore in the optimum size showed 29% extraction where the random combination of particle sizes had 20% extraction.

4.3 Sequential extraction

This study was to determine the amount of each fraction of existing copper in the ore. The method was detailed in Chapter 3. The results of this study are presented in Figure 4-14. The control used in this test was distilled water and the concentration of biosurfactant was optimal (2% rhamnolipid, 1.5 g ore in 15 mL of solution, pH=6, particle size between 0.15 mm and 0.3 mm) and the test was performed for 6 days.

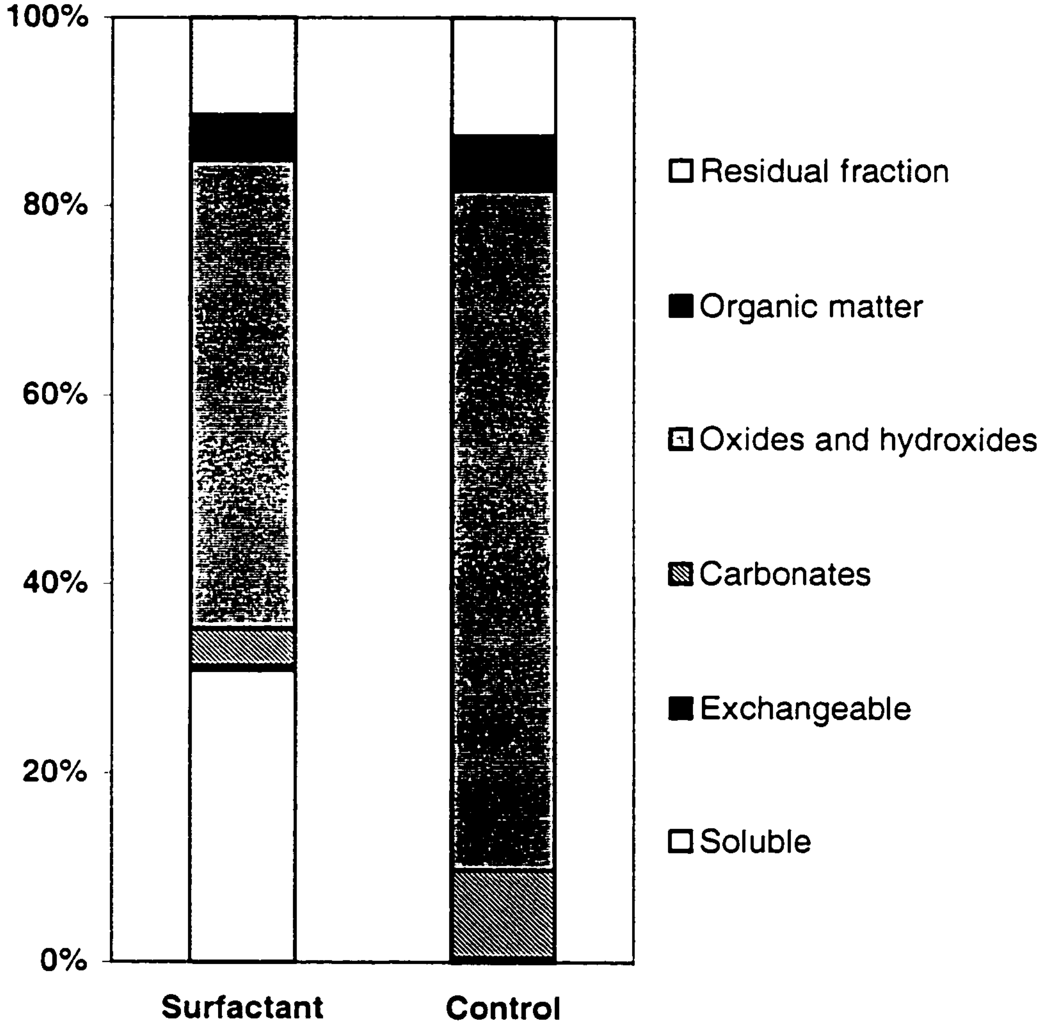


Figure 4-14 Sequential extraction of copper from ore after rhamnolipid and water (control) washing

The sequential extraction study shows the exchangeable portion in ore is very small that means ion exchange does not play a major role in the copper extraction process by rhamnolipid. The figure (Fig. 4-14) also shows that carbonate and oxide and hydroxide portions are the major sources of copper in the ore and the rhamnolipid is able to extract a significant amount of copper from these fractions.

Chapter 5

Conclusions

5.1 Conclusion of this study

This research was performed to evaluate the application of rhamnolipid on extraction of copper from mining residue. The residue, or ore, initially has a very small portion of copper, 8.95 g copper in 1kg ore (Table 4-1) that cannot be economically removed. From an environmental point of view, the existing copper in the ore is a heavy metal contaminant and should be removed so that it will not impact the environment.

This study dealt with several chemical and physical factors involved in the extraction to find the best condition for the extraction. These parameters were ore particle size, pH, concentration of biosurfactant, and the mass to volume ratio of copper in rhamnolipid. Effect of NaOH, shaking, and the use of several washings were tested and the results are shown in the following table (Table 5-1).

Table 5-1 The optimum conditions to extract copper from residue

Factor	Optimum value
Particle size	0.15 mm - 0.3
pH	6
Concentration without NaOH	5% but is too viscous to work, 2% is recommended
Concentration with NaOH	2%
Volume of rhamnolipid for 1.0 g ore	10 mL
Time	6 days, after it the extraction rate drops
Several washings	After 6 day the extraction drops to less than 3%

The importance of size was in the contact surface area between the ore particle and the biosurfactant. Smaller particles provided a bigger surface area but they had more contact points between each other that became critical when the number of particles was very big for a certain volume/weight of particle.

The sequential extraction (Fig. 4-14) shows a large amount of extracted copper belongs to oxide and hydroxide fractions. Since the solubility of hydroxide copper is maximum at pH 6 (Fig. 4-5), the same pH for the extraction was found in this study, as predicted.

Extraction of 1.0 g ore with various volumes of rhamnolipid (Fig. 4-7), shows if 10 mL solution is used for each gram of ore, the extraction will be maximal and increasing the biosurfactant volume does not enhance the extraction.

Time was a difficult parameter to be optimized because in the long term processes like ore extraction, the difference between the extraction in two days was not significant. In this study, therefore, 6 days was chosen since after 6 days the rate of extraction became less than 1% per day.

NaOH makes a remarkable improvement in extraction when used with 2% or less rhamnolipid concentration compared with rhamnolipid without any additives. At higher concentrations of rhamnolipid, adding NaOH decreases the extraction (Fig. 4-10). This additional amount of extracted copper does not belong to the exchangeable fraction of copper since sequential extraction shows this part is less than 1% (Fig. 4-14).

Several washes could help the extraction process. The study shows a possible relative 10% (3% in total) or more extraction with six times washing compared with one time washing (Fig. 4-12). Since the effect of volume was investigated earlier (Fig 4-7) it is known that there is no difference in extraction when the volume exceeds 10 mL for 1.0 g ore. This additional copper is, therefore, a result of adding fresh solutions.

Overall, with using ore particles with a random distribution of sizes under the optimized conditions, the total extraction becomes 24% (Fig. 4-12) which shows a relative improvement of 24% (6% in total) relative to the optimized size of particle used (Fig 4-2).

5.2 Suggestions for future studies

- Investigation of the potential for rhamnolipid to extract other heavy metals from ores.
- Evaluation of other surfactants or mixtures of several surfactants for metal extraction from ores.
- Evaluation of *in situ* production of biosurfactants to increase metal extraction from ore.

5.3 Contribution to knowledge

- Evaluation of the potential of biosurfactants (rhamnolipid) with low toxicity to extract heavy metals (copper) from a mining ore and enhance the percentage of extraction with NaOH.
- Correlation of ore washing procedures with sequential extraction studies to find which fractions are involved in the copper extraction. For example, rhamnolipid in this study extracts copper mostly from oxide and hydroxide fractions.

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