

**REMOVAL OF HEAVY METALS FROM
WASTEWATERS BY
ION FLOTATION**

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(Environmental Pollution and Control)**

by

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ABSTRACT

In this study, ion flotation experiments were performed to investigate the removal of heavy metals (copper, zinc, silver and chromium) from wastewaters. Various parameters such as pH, surfactant and frother concentrations and airflow rate values were tested to determine the optimum flotation conditions. Sodium dodecyl sulfate and Hexadecyltrimethyl ammonium bromide were used as collectors. Ethanol / MIBC were used as frothers.

For 10 mg/L initial concentrations of copper, zinc, silver and chromium (III), the highest recoveries obtained were 90%, 71%, 73% and 97%, respectively. When the initial concentration of metals increased the recovery decreased. This proves the attachment of metal ions on surfactant molecules.

The presence of Na^+ , Mg^{2+} , Ca^{2+} ions in solution reduced the recoveries in case of all the metals since the presence of excess Na, Mg, Ca ions compete with metals and the metal ions can not find enough surfactant molecules to attach to.

Selective flotation experiments were conducted in the presence of metal ion mixture solutions. It was possible to separate copper and chromium from zinc and silver, and also possible to separate chromium from zinc and copper and zinc from copper and chromium under suitable conditions.

The classical first order equation fitted the results on flotation. Zinc and chromium floated not only more in an amount but also floated faster than copper.

Surface tension measurements were conducted to investigate both the collector surfactants and the frothers at air/water interface since air bubbles carry the surfactant-metal ion complexes to the froth and separate from solution.

ÖZET

Bu çalışmada, ağır metallerin (bakır, çinko, gümüş, krom) iyon flotasyonu kullanılarak atıksulardan uzaklaştırılması araştırılmıştır. Optimum flotasyon koşullarının belirlenebilmesi için çeşitli pH, yüzey aktif madde, köpük sağlayıcı derişimleri ve hava akış oranı test edilmiştir. Sodium dodecyl sulfate (SDS) ve Hexadecyltrimethyl ammonium bromide (HTAB), yüzey aktif madde olarak, etanol ve MIBC köpük sağlayıcı olarak kullanılmıştır.

Yapılan deneylerde 10 mg/L bakır, çinko, gümüş ve krom giderimi için sırasıyla %90, %71, %73 ve %97' lik verimler elde edildiği görülmüştür. Metallerin başlangıç konsantrasyonları arttırıldığında yüzey aktif madde molekül sayısının yetersizliğinden dolayı verimleri düşmektedir. Bu yüzey aktif madde molekülü ile metal iyonu birleşiminin bir göstergesi olarak görülebilir.

Çözeltide sodyum, kalsiyum ve magnezyum iyonlarının bulunması bu iyonların metal iyonlarıyla yarış içinde olmasından ve yeterli sayıda yüzey aktif madde molekülü olmadığından flotasyon verimini düşürmektedir.

Koşullar ayarlandığında bakır ve kromun, gümüş ve çinkodan ayrılması mümkündür. Yine koşullar ayarlandığında kromun çinko ve bakırdan oluşan çözeltiden ayrılması da mümkündür. Bir diğer koşulda da çinko, bakır ve krom karışımından oluşan çözeltiden ayrılmıştır.

DeneySEL bulgular klasik birinci derece flotasyon modeline uymaktadır. Çinko ve krom sadece miktar olarak değil yüzme hızı olarak da bakırdan daha hızlı yüzmektedir.

Flotasyonda oluşan yüzey aktif madde-metal iyonu komplekslerini su yüzeyine taşıyan hava kabarcıkları olduğundan, hem yüzey aktif madde toplayıcıların hem de köpük yapıcıların hava/su ara yüzeyindeki etkilerini incelemek için yüzey gerilim deneyleri gerçekleştirilmiştir.

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CHAPTER 1

INTRODUCTION

1.1. Statement of the Pollution Problem

Due to increase in the world population and development of industrial applications, environmental pollution problem became important. Communities produce both liquid and solid wastes. The liquid waste-wastewater- is essentially the water supply of the community after it has been used in a variety of applications. The presence of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. The amount of heavy metals that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment.

In Turkey , the situation is not so different from highly industrialized countries. In recent years, heavy metal concentrations, besides other pollutants, have increased to reach dangerous levels for living environment in many regions of Turkey. The wastewater discharges such as those from the metal plating industries, are the main sources of metal pollution and therefore the level of pollution is much higher in industrialized regions.

Heavy metals are elements such as Cu (Copper), Zn (Zinc), Ag (Silver), Cr (III) (Chromium), Hg (Mercury), Cd (Cadmium), Fe (Iron), Co (Cobalt), As (Arsenic) which are usually associated with toxicity. Among them only Cu, Zn, Ag and Cr will be studied in this thesis. Copper is present in wastewaters of most industries such as metal cleaning and plating baths, mining and acid mine drainage, petroleum refining, paint and pigment manufacturing, motor vehicle and aircraft plating and finishing, copper ore extraction in different ranges from 0.12 mg/L to 183 mg/L (Table 1.1). Industries which contain significant levels of zinc include steel works with galvanizing lines, zinc plating, acid mine drainage, plating and metal processing, paint and manufacturing, textile dyeing, pigment manufacturing. In waste waters of industries, zinc values were reported to range from 0.01 mg/L to 1,702 mg/L (Table 1.2.). Silver is a naturally occurring metal that is extensively utilized in the photographic and imaging industry, as

well as in electronics and electrical applications and other lesser uses. It is known to be discharged to the environment from its industrial applications, and this leads to the possibility for exposure to aquatic organism (Purcell et al. 1997). Silver values were reported to range from 100 mg/L to 300 g/L (Table 1.3.) in such waste waters. Chromium is considered as a highly toxic water pollutant. Chemical industries, leather, paint and cement industries produce high content chromium wastes that are ranged from 0.01 to 30 mg/L (Table 1.4.).

Table 1.1. Copper Levels Reported in Industrial Wastewaters
(Source: Metcalf and Eddy 2003)

Industrial Source	Copper Concentration (mg/L)
Paint and pigment manufacturing	0.04-100
Motor vehicle and aircraft plating	0.5-33
Copper plating baths	2.2-183
Acid mine drainage	0.12-128
Petroleum refining	0.0-1.4
Copper ore extraction	0.28-20

Table 1.2. Zinc Levels Reported in Industrial Wastewaters
(Source: Metcalf and Eddy 2003)

Industrial Source	Zinc Concentration (mg/L)
Metal processing	0.2-1,000
Zinc plating	2-1,050
Paint manufacturing	0.3-77.4
Textile dyeing	2-6
Pigment manufacturing	0-1,702
Steel works	2.1-1,210

Table 1.3. Silver Levels Reported in Industrial Wastewaters

(Source: WEB_1 2003)

Industrial Source	Silver Concentration (mg/L)
Photographic manufacturing	100-260000
Steam wells	100-300000
Oil well brines	10-100

Table 1.4. Chromium Levels Reported in Industrial Wastewaters

(Source: Metcalf and Eddy 2003)

Industrial Source	Chromium Concentration (mg/L)
Chemical industries	1.1-17.7
Leather industries	1.7-55
Paint industries	2.5-30

In order to reduce the pollution problem in environment that is caused by these heavy metals, their concentrations must be reduced before discharging to obey the wastewater standarts listed in Table 1.5. So, an effective treatment process must be applied.

Table 1.5. Wastewater Standarts

(Source: WEB_2 2004)

<i>Metal Ion</i>	Maximum Allowable Value, (mg/L)*
Copper	1
Zinc	5
Silver	0.2-2.0µg/L
Chromium	0.5

1.2. Health Effects

Heavy metals are released into the environment by activities of people and high levels of these metals constitute a great risk for the aquatic ecosystem and human. Health effects of Cu, Zn, Ag, and Cr are listed in Table 1.6.

Table 1.6. Health Effects of Heavy Metals
(Source: WEB_3 2003)

Copper	nausea,vomiting,abdominal pain, damage the liver and kidneys.
Zinc	stomach cramps,nausea, vomiting, anemia, pancreas damage.
Silver	nausea, vomiting, skin irritation, damage the liver, kidney, eyes, lung and brain
Chromium	irritation to the nose, cause stomach upsets and ulcers, kidney and liver damage.

1.3. Common Methods Used to Remove Heavy Metals from Industrial Wastewaters

Methods such as chemical precipitation, solvent extraction, reverse osmosis, ultrafiltration, electrodialysis, ion exchange are used commonly to remove heavy metals from wastewater to day. The summary of these methods will be given in the following paragraphs.

1.3.1 Chemical Precipitation

Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation. Chemical precipitation is employed for most of the metals. Common precipitants include hydroxide (OH)⁻ and sulfide (S²⁻). Metals are precipitated commonly as metal hydroxides through the addition of lime or caustic to a pH of minimum solubility. In practice, the minimum achievable residual metal concentrations are also dependent on the nature and concentration of the organic matter in the wastewater as well as the temperature. However, this method is inappropriate for large solution volumes with

very low concentrations of metal ions. Precipitating hydrous oxides of the metals with lime and soda (NaOH) is used in removal of heavy metals. The cost of most of the coagulants, chemical and polyelectrolytes used for precipitation of the metals, in the conventional methods, makes the process economically unattractive. Precipitation generates large amounts of sludge, which is costly to dispose of and often hazardous besides requiring long settling times despite the use of coagulants (Metcalf and Eddy 2003).

1.3.2. Ion Exchange

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Materials used for the exchange of metals include zeolites, weak and strong anion and cation resins, chelating resins. Ion exchange processes are highly pH-dependent. Solution pH has a significant impact on the metal species present and the interaction between exchanging ions and the resin. Operating and wastewater conditions determine selectivity of resin, pH, temperature, other ionic species and chemical background. The presence of oxidants, particles, solvents and polymers may affect the performance of ion exchange resins (Eckenfelder 2000).

1.3.3. Reverse Osmosis

Reverse osmosis is used for the removal of dissolved constituents from wastewater remaining after advanced treatment. When two solutions having different solute concentrations are separated by a semipermeable membrane, a difference in chemical potential will exist across the membrane. Water will tend to diffuse through the membrane from the lower concentration side to the higher concentration side. In a system having a finite volume, flow continues until the pressure difference balances the chemical potential difference. This balancing pressure difference is termed the osmotic pressure and is a function of the solute characteristics and concentration and temperature. If a pressure gradient opposite in direction and greater than the osmotic pressure is imposed across the membrane, flow from the more concentrated to the less concentrated region will occur and is termed reverse osmosis (Metcalf and Eddy 2003). Reverse osmosis has been proposed for treatment for recovery of heavy metals. To protect the reverse osmosis membranes, feed solution pH must be adjusted. Reverse

osmosis alone will not achieve complete recovery and reuse of the solutions. Pretreatment required prior to the reverse osmosis unit includes equalization, media filtration, pH adjustment and antiprecipitant additions.

1.3.4. Ultrafiltration

Ultrafiltration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultrafiltration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary in this method uses more electricity, may need pretreatment, requires replacement of membranes. (Eckenfelder 2000).

1.3.5. Electrodialysis

In the electrodialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the electrodialysis process for wastewater renovation include chemical precipitation of salts with low solubility on the membrane surface. To reduce the membrane fouling, activated carbon pretreatment, possibly preceded by chemical precipitation and some form of multimedia filtration may be necessary (Metcalf and Eddy 2003). The electrolytic process has not been widely utilized in full-scale treatment of metal wastes.

1.4. Scope of the Study

The scope of this study was to investigate the removal of heavy metals especially copper, zinc, silver and chromium which are highly toxic metals, from industrial wastewaters by ion flotation. The objective of this investigation is to establish the optimum ion flotation conditions in terms of pH, surfactant concentrations, ethanol concentrations, airflow rate values in order to remove metals effectively and selectively from wastewaters.

CHAPTER 2

ION FLOTATION

For 100 years, the separation and preconcentration bubble methods called *flotation* has been used in mining and metallurgical industry to operate valuable minerals from natural resources. Apart from mining aims, these techniques have found great application for separating and removing many kinds of harmful impurities from different polluted water systems. Today, there are several attempts to apply flotation (Pavloska 2003).

There are many differences between an industrial flotation processes, where the materials floated are the relative massive grains of ores and flotation as an analytical method, where the particles are invisible ions or molecules. However for both procedures the same principles and laws are valid (Caballero 1990).

Ion flotation is a comparatively novel separation technology, first described by Sebba in 1959, for recovering and removing metal ions from dilute aqueous solutions (Bernasconi 1998 ; Jdid and Blazy 1990 ; Matis and Mavros 1991 ; Tessele 1998). This process involves the removal of surface inactive ion species from aqueous solution by adding the proper long chain surface active agent of opposite charge to the ion to be separated. A surface active reagent, known as collector, is added to the solution to be treated and adsorbs at the solution – gas interface. After the subsequent passage of gas bubbles through the solution, surfactant and ions are accumulated at the gas/liquid interfaces and are carried into a foam or froth, rising above the solution. The froth is swept from the top of the flotation cell. Appropriate surfactants prevent bubble rupture and promote the formation of a foam (Zouboulis 1995).

Ion flotation is a complex process which occur in a multi-component, multi-phase system. A schematic representation of various sub-processes which take place during flotation is given in Figure 2.1. The figure shows the three dispersed phases in the flotation cell, namely, metal ions, surfactant molecules and air bubbles, and their interactions with each other. Water is considered to be the continuous medium in which the interactions take place and is therefore not shown in Figure 2.1. It is also assumed that these interactions take place under an unchanging set of hydrodynamic conditions.

Chemical and physical properties of each dispersed phase affect the overall flotation response through various sub-processes. A detailed discussion is presented in the following paragraphs.

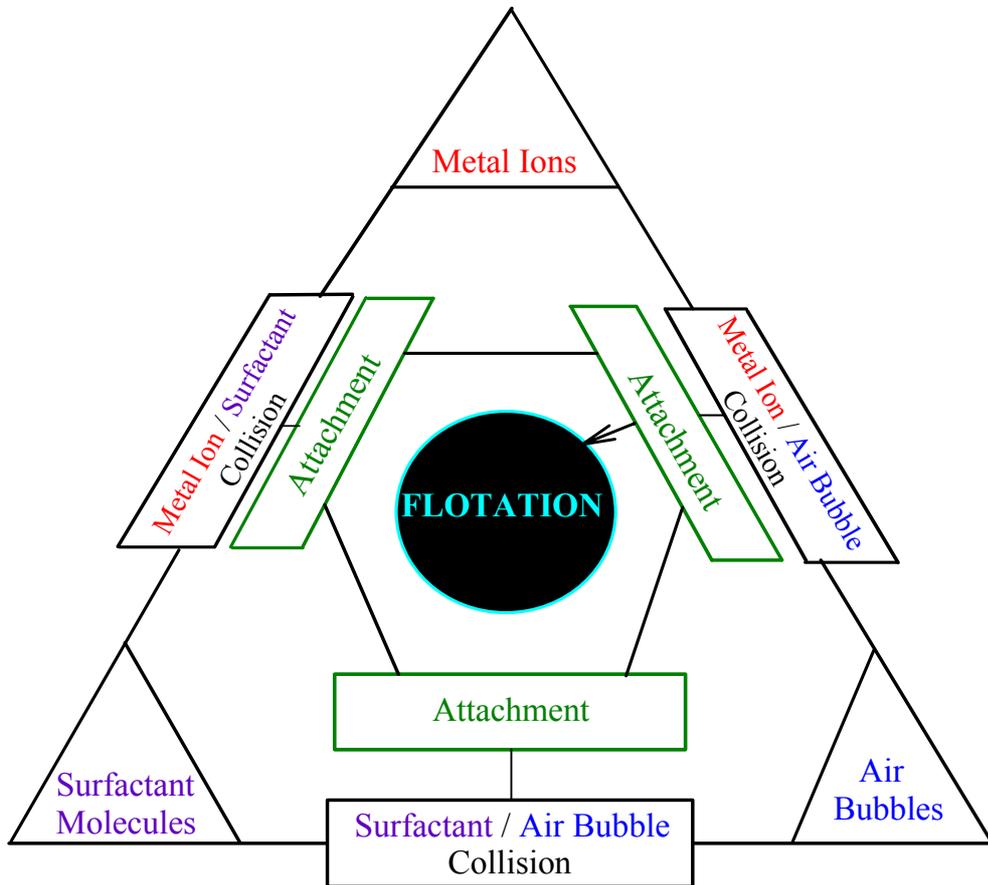


Figure 2.1. A Schematic Representation of Various Sub-Processes in Ion Flotation

2.1. Dispersed Phases

2.1.1. Metal ions

In aqueous solution free metal ions are complexed with water and these are said to be hydrated. The interaction of hydrated metal ions with acids and bases is a ligand exchange reaction which is called hydrolysis. It describes general reaction in which a proton is transferred from an acid to water or from water to base. This type of reaction which involves hydrated metal cations as the proton-donors or acids occurs readily. The hydrolysis of metal ions is a stepwise replacement of coordinated molecules of water of hydration by hydroxyl ions. This replacement forms by the transfer of protons from waters of hydration to free water molecules to occur an hydronium ion. The hydrolysis reactions depicted as acid-base (proton transfer) reactions. Because of this, the pH of the system will influence the distribution of the various species. In general, the percentage of the hydrolyzed species increases as the pH increases, while the concentration of a conjugate base would increase if the pH of a solution containing its conjugate acid were raised. All heavy metal ions, used in this study, form complexes with numerous ligands that are present in water and wastewater. Forms of these metal ions in aqueous solution will be shown and explained with details in Chapter IV. And now physical properties of metal ions need to be known that understanding these ions. The physical properties of metal ions, that are copper, zinc, silver and chromium, are given in Table 2.1. (Greenwood 2003).

Table 2.1. Physical Properties of Metal Ions
(Source: Greenwood 2003)

Properties	Copper	Zinc	Silver	Chromium
Atomic weight	63.55	65.39	107.87	51.99
Electronegativity	1.9	1.6	1.9	1.6
Metal radius (12-coordinate) / pm	128	134	144	128
Effective ionic radius (6-coordinate)/pm	73	74	94	61.5
Melting point (°C)	1083	420	961	1900
Boiling point (°C)	2570	907	2155	2690
Density (20°C) g/cm ³	8.95	7.14	10.49	7.14

2.1.2. Surfactant Molecules

The term soap is applied to the sodium or potassium salts of long – chain fatty acids that are but one example of a general class of substances called *amphiphiles*. Those are substances whose molecules consist of two well-defined regions : one which is oil-soluble (hydrophobic, lipophilic..) and one which is water soluble (hydrophilic). The hydrophobic part is non-polar and usually consists of aliphatic or aromatic hydrocarbon residues. The hydrophobic character is not much affected by introducing halogens and similar groups (Laughlin 1981). The hydrophilic part consist of polar groups which can interact strongly with water (especially hydroxyl, carboxyl and ionic groups). Typical examples are;

$C_{19}H_{42}NBr \rightarrow$ Hexadecyltrimethyl Ammonium Bromide

$CH_3(CH_2)_{11}O.SO_2O^-Na^+ \rightarrow$ Sodium Dodecyl Sulphate

$CH_3(CH_2)_{13}.O.SO_2O^-Na^+ \rightarrow$ Sodium Tetradecyl Sulphate

The most significant characteristic of this type amphiphile tends to adsorb very strongly at the interface between air and water, thus the hydrophobic part of the molecule can escape from the aqueous environment when the hydrophilic head group can remain in the water. Such substances are said to be strongly surface active because they lower the surface tension. Therefore they make the formation of new surface easier and are widely used as foaming and dispersing agent (Hunter 2001).

Depending on the nature of hydrophilic group, surfactants are classified as (Rosen 1989) ;

- **Anionic** : The surface active portion of the molecule bears a negative charge.
- **Cationic** : The surface active portion of the molecule bears a positive charge.
- **Zwitterionic** : Both positive and negative charges may be present in the surface-active portion.
- **Nonionic** : The surface active portion bears no apparent ionic charge.

For surfactants having not only hydrophilic part but also hydrophobic part causes some effects such as ;

Increase in the length of the hydrophobic group decreases the solubility of the surfactant in water and increases its solubility in organic solvents, increases the tendency of the surfactant to adsorb at an interface or to form micelles, increases the melting point of the surfactant and sensitivity of the surfactant, if it is ionic, to precipitation from water by counterions (Rosen 1989).

At very low concentrations ($<10^{-4}$ M) many surfactants are soluble in water to form simple solutions. Some of the molecules will also be adsorbed at the surfaces of the solution. As the concentration rises adsorption becomes stronger until saturation is reached when the molecules are packed close together with strong lateral interactions occurring between the hydrophobic chains. At this point formation of micelle is important. These are structures in which the hydrophobic portions of the surfactant molecule associate together to form regions. The hydrophilic groups remain on the outer surface to maximize their interaction with the water and the oppositely charged ions (called counter ions). A significant fraction of the counterions remains strongly bound to the head groups so that the repulsive force between those groups is reduced. The structure of the micelle depends upon the temperature and concentration but also on the details of the molecular structure : size of head group, length, number of hydrocarbon chains, presence of branches, etc. (Hunter 2001).

The concentration at which micelles first form in the solution is called the critical micellization concentration (c.m.c.). Micellization is an alternative mechanism to adsorption at the water, thereby reducing the free energy of the system. It's marked by quite sharp changes in slope when various transport and equilibrium properties are plotted against concentration. The long chain fatty acid soaps and simple detergents like sodium dodecyl sulphate (SDS) initially form micelles that are spherical in shape. As the surfactant concentration is increased above the c.m.c., the initially spherical micelles become more distorted in shape, forming cylindrical rods or flattened discs (Hunter 2001).

For surfactants with a single straight hydrocarbon chain, the c.m.c. is related to the number of carbon atoms in the chain.

One of the most surprising things about micellization is the very weak temperature and pressure dependence of the c.m.c., considering that is an association process (Lindman and Wennerström 1980). Raising the temperature has a quite different effect on ionic and non-ionic surfactants. For ionics, there is a temperature below which the solubility is low and solution appears to contain no micelles. Above

this temperature micelle formation becomes possible and there is an increase in solubility of the surfactant. It is significant that surfactants are less effective below this point.

Foam height generally increases with increase in surfactant concentration below the c.m.c. until the c.m.c. is reached, foam height reaches a maximum value somewhat above the c.m.c. The lower c.m.c., the more efficient the surfactant as a foamer. Surfactants with longer hydrophobic groups are more efficient, but not necessarily more effective, foaming agents. The effectiveness of a surfactant as a foaming agent appears to depend on both its effectiveness in reducing the surface tension of solution and on the magnitude of its intermolecular cohesive forces. The lower the surface tension of the aqueous solution the greater appears to be the volume of foam of the same average bubble size produced (Rosen 1969).

2.1.3. Air Bubbles

Air bubbles are introduced into the system to capture and carry hydrophobic particles to the froth phase leaving hydrophilic ones selectively behind. In a typical flotation cell the bubble size ranges from about 0.5 to 1.0 mm. When bubble size is reduced, the number of bubbles in the system will increase for the same volumetric air flow rate and should result in higher flotation rates. Frothers are usually employed to prevent bubble coalescence and to increase the stability of the froth.

Bubbles can be generated in liquids by several different methods, for example;

- An increase in temperature to cause boiling at first, dissolved gases are released, and ultimately vapour- filled bubbles are generated.
- A decrease in pressure to cause precipitation of bubbles.
- A mechanical agitation to cause gas entrapment.
- An injection of gas through an orifice or a porous membrane.

Once formed within a pure liquid, bubbles tend to coalesce (to reduce the extent of total surface area and thus the overall amount of free energy in the system) and (if free) to rise in the liquid under the effect of buoyancy. Both the coalescence by surface active impurities and the rise by attachment to a hydrophobic surface (Leja 1982).

2.1.3.1. Foams and Froths

When two bubbles come in contact with each other, liquid film between them thins and breaks, causing bubbles to coalesce, unless excess surfactant is present at their interfaces or the time of contact is too short. Bubble coalescence can be studied either on two bubbles grown in solution by blowing compressed gas through a fine glass frit (Sagert 1976).

When coalescence of bubbles formed in a liquid does not take place in fractions of seconds, the bubbles rise to the surface and aggregate, forming a foam or a froth. The terms foam and froth are sometimes used interchangeably; however, the imperfectly drained liquid - bubble systems, generally unstable, are called foams, better drained bubble systems are referred to as froths. Two phase froths are obtained with solutions of ionized surfactants (Leja 1982).

There is a strong correlation between the viscosity of liquid and the stability of foam. The more viscous the liquid into which the bubbles are injected, the slower is the drainage of liquid from layers between the bubbles. In pure viscous liquids of different surface tension showed that the rate of collapse was the same for all systems when their viscosities were made equal by keeping each system at an appropriate temperature. The values of surface tension wasn't a critical factor in these foams (Clift et al. 1978).

Foams and froths are thermodynamically unstable, since the free energy of the system decreases when they collapse. The lifetime of foam or froth depends on a number of surface chemical and physical parameters, namely concentration of surfactants, surface viscosity and transport, all of these, in turn, are determined by the molecular structure of the surfactant used and interactions between surfactants, solutes and water molecules.

2.1.3.2. Theories of Foam and Froth Stability

The most important factor in the formation of foam is the presence of a surfactant at the liquid/gas interface. The effectiveness of different surfactants is assessed by measuring the foam lifetime (stability). This is done by several methods, such as; When air is injected at a given rate into a solution, or mechanical, when the solution is agitated with a propeller, etc. In each instance, the air is dispersed for a given length of time, at the end of which the volume of froth is estimated and its decay with time measured (Leja 1982).

A significant feature of all frothers used in flotation systems is their nonionic polar group. Characteristic of the better-acting frothers is the nonadlineating structure of their nonpolar groups. All n-alkyl hydrocarbon chains of surfactants readily develop multiple van der waals bonds, that is, become adlineated. This adlineation occurs, if the polar groups associated with the chains aren't much larger than the cross section of the hydrocarbon chain itself. The bubbles themselves are always charged, whether in pure water, in solutions of organic electrolytes, or in solutions of surfactants. Owing to a preferential adsorption of OH^- , there is a definite pH dependence of their charge, whether in water or in nonionic surfactant solutions. In view of these features, there is a high probability that similarly charged hydrophobic ions and bubbles will be colliding with each other in a flotation cell (Jones et al. 1984).

The main role of frother-acting surfactant in flotation is to provide means of replacing repulsive forces, whenever necessary, with attraction, owing to the ability of such surfactant molecules to align their dipoles appropriately at the moment of ion-bubble collision.

It is from ability to align their dipoles that nonionic surfactants with nonadlineating hydrocarbon groups prove themselves the better frothers. The interaction with the collector species is beneficial, but not always so. When it is so strong that it prevents dipole realignment, collisions may result in no attachment (the respective polar groups are then lockes together). On the other hand, even a strong interaction between collector and frother species may allow an attachment to take place but no froth is generated because the nonpolar groups of the reacting frother-collector molecules form an adlineated film. Surfactants with charged polar groups may act as frothers but only in situations under which ions are oppositely charged with respect to the charge on the bubbles. Such conditions are not likely to be met in practice over an extensive range of concentrations or pH. It is ,however, that some charged surfactants are capable of acting in a dual capacity as a collector and a frother by virtue of providing a sufficient quantity of neutral products through reactions with counterions (Leja 1982).

2.2. Sub-Processes

The three dispersed phases interact through collision, attachment and detachment sub-processes which could occur simultaneously or sequentially depending on the environmental conditions. The physical and chemical properties of each dispersed phase determine the outcome of each sub-process, hence, the flotation response. In the following paragraphs a detailed discussion of these interactions is presented.

2.2.1. Collision

The major physical properties which influence the collisions probability between the three dispersed phases are the size, number, density and shape. Efficiency of collision may be defined as the ratio of particles (metal ions, surfactant molecules or air bubbles) colliding with a given body to those flowing across the projected collision cross sectional area of that body. A successful collision only means that the two bodies have approached within a certain distance and may, or may not, result in attachment.

2.2.2. Attachment

A successful attachment between the two members of any of the dispersed phases given in Figure 2.1 requires that the water film between them should drain out within the time frame of collision. Probability of adhesion could be defined as the fraction of the colliding particles which would adhere to the body upon which they impact. Similar to the collision probability, a separate adhesion probability may be defined for each surfactant molecule/metal ion, surfactant molecule/air bubble and metal ion/air bubble pairs. While the collision probability is mainly affected by the physical properties of the particles, the adhesion probability is determined by both the physical and chemical properties of the impacting particles.

Attachment or coalescence sub-processes between similar dispersed phases, bubble/bubble, may be detrimental to flotation since the dispersed forms of this phase are required for maximum in flotation.

2.3. Effect of Surfactants on Various Sub-Processes

A variety of reagents might be used to modify the surface properties of the dispersed phases given in Figure 2.1. The reagents capture metal ions and also adsorb at air/water interface and influence the outcome of the sub-processes, hence, flotation. As a result the role of surfactants in flotation is very complex. The mechanism and quantity of adsorption at air/water interface will be determined by factors such as surfactant type, concentration and conditioning.

2.3.1. Surfactants and Metal Ion / Surfactant Molecule Attachment

The key to flotability of chemical species is hydrophobicity. Substances are rendered hydrophobic by addition of the suitable collector, in which polar groups are eliminated by reaction leaving non-polar groups exposed to solution. These groups can be adsorbed on the liquid / gas interface (Matis et al. 1995).

The anionic surfactant, with its negative – charged part, adsorbs onto the ions while its hydrocarbon chain amplifies hydrophobic character of the precipitate. As a result of that interaction the gas bubbles passing through the system attached very well onto the hydrocarbon chain and the separation of the ions from the liquid phase. Figure 2.2a shows no attachment of a metal ion on air bubble in the absence of a surfactant, 2.2b shows an attachment of a metal ion in the presence of a surfactant.

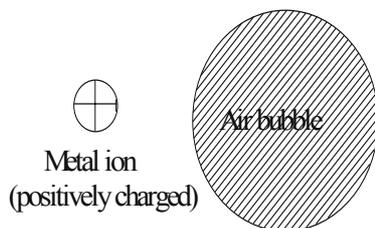


Figure 2.2a. No attachment in the absence of surfactant (SDS)

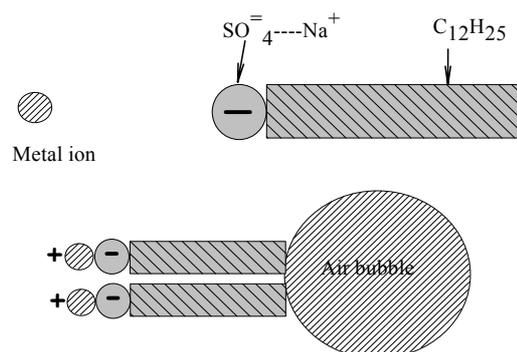


Figure 2.2b. Attachment in the presence of surfactant

The quantity of collector used in ion flotation is also important. Usually small excess of collector is added to have maximum removal of metallic ions in solution. Excessive surfactant should be avoided not only due to higher cost, but also because of other effects, such as large foam losses and the potential toxicity of residuals amounts of collector in the effluent.

2.3.2. Surfactants Adsorbed at the Air/Water Interface

Adsorption of a surfactant at the air/water interface results in finer bubbles and a stable froth and therefore affects the collision and adhesion sub-processes. This is one of the most frequent use of water soluble surfactants in flotation (frothers). Some commonly used frothers in flotation are MIBC (methyl isobutyl carbinol), ethanol, methyl ethers (e.g., Dowfroth 250), polypropylene glycol, dodecylamine. Many commercial frothers are known to have both frothing and collecting properties. The creation of a finer bubble size distribution through changes in dynamic surface tension is also a very important result of frother addition. However, similar to collector chemicals, higher concentrations of frothers should be avoided (Duyvesteyn 1993; Alexandrova 1996).

2.4. Inorganic Agents, Activators, Depressants

The purpose of making an addition of any reagent to a flotation system is to improve floatability of the desired ion at the desired moment to achieve selectivity of separation. The additives are grouped under different headings, depending on their action. Thus, these additives, inorganic or organic in nature, which,

- Control the pH of the system
- Regulate the oxidation states of ions in solution of surfactants used as collectors
- Control the concentration of metallic ions in solution and at interfaces through precipitation or complexing with HS^- , CN^- , OH^- , etc...

Additives which are more specific in their action are called *activators*. Reagents which have a specific opposite effect to activators are called *depressants*. It is obvious that the same chemical species may act as a regulatory agent or an activator, or a depressant, depending on the character of the flotation system. At the same time, depending on the concentration, it is reducing agent and a highly selective charge density regulator (Leja 1982).

2.5. pH of the System

The type of additive used to control the pH is often of paramount significance. Although an acidic pH can be obtained by HCl, H₂SO₄, HNO₃, etc... the price is not the criteria to follow in deciding which additive to use, since the side effects of Cl⁻, SO₄²⁻, NO₃⁻ ions may play a very significant role in some systems. The solution pH determines the extent of hydrolysis of surfactants. This, in turn, either helps or hinders the adsorption of the surfactant at the various ionized liquid interfaces, contributing to greater or lesser selectivity of flotation (Scorzelli 1999).

Metal cations exist in aqueous solutions primarily as complexes of H₂O molecules and OH⁻ ions; when the oxidation state of the metal cation is higher, in addition to hydroxyl complexes some OXO (containing O²⁻ as a ligand) complexes appear in the pH range 4-10. Because of the limited pH range of aqueous solutions, not all of the possible metal complexes can exist as an ionic hydroxyl or OXO complexes. Polymerization of hydrolysis species results in the formation of colloidal hydroxyl polymers. These species are bonded through OH bridges or through O bridges. The extent of hydrolysis depends on the pH and total concentration of metallic ion. Two ways of graphing the distribution of complexes can be drawn, either as a percent mole fraction of individual species at each pH or as relative intermediate S curves. A third way of graphing the relationship between pH and hydrolysis species can be plotted with the log concentration of each hydrolysis species versus the pH for a thermodynamic equilibrium between species. When the solution becomes oversaturated with respect to Mⁿ⁺(OH)_n - depending on the kinetics of precipitation - a colloidal hydroxide is present in addition to the hydrated complexes in solution (Leja 1982).

When simplified systems containing individual ions in solution are tested in collector at different pH, the comparison of results may indicate definite differentiation in collector adsorption. This would suggest that flotation of ions should occur in different pH ranges, giving rise to selectivity controlled by pH.

2.6. Literature Survey

Charewicz et al. 1999 examined the batch flotation of zinc (II) and silver (I) ions from dilute aqueous solutions with sodium dodecyl sulphate and ammonium tetradecylsulfonate as anionic surfactants and with cetylpyridinium chloride as a cationic surfactant. Also, they studied the effect of inorganic ligands (thiosulphates,

thiocyanates) on the selectivity of ion flotation of Zn (II) and Ag (I) ions. They found that Zn (II) and Ag (I) could be separated from diluted acidic aqueous solutions with anionic surfactants since Zn^{2+} cations exhibited a much higher affinity for a surfactant than did Ag^+ cations. The separation of metal ions was also possible when solution contains thiosulphate or thiocyanate ligands.

A thermodynamic approach was investigated to model the removal of cupric ion from (sodium dodecyl sulphate) SDS-Cu, (sodium tetradecylsulphate) STS-Cu and (sodium hexadecylsulphate) SHS-Cu ion flotation systems by Liu et al. 2001. They obtained surface tension data a wide concentration range of each alkylsulphate-copper solution. They used the data to fit analytical regression equation and differentiated to generate an expression for the metal ion adsorption densities. They demonstrated that the more active collectors gave faster metal removal kinetics and were capable of attaining much lower steady-state copper concentrations and they built up a model for the copper removal kinetics.

Liu et al. 2000 developed theoretical models to find the selectivity coefficients for Ca^{2+} / Cu^{2+} and Pb^{2+} / Cu^{2+} in ion flotation by using SDS as the collector. Also, they studied to improve surface tension model using surface tension data for the metal-SDS ion flotation systems. Other important thing for this study was to calculate theoretically the dehydration parameter and dehydration Gibbs free energy using geometric considerations. Then this incorporated into a Grahame adsorption equation to derive a selectivity coefficient for two metal ions at the solution-vapour interface. Finally they concluded the dehydration model gave a good prediction of the selectivity coefficients this was not the same in the surface tension model.

Zouboulis et al. 1995 investigated the recovery of silver from dilute aqueous solutions containing complexing agent by ion flotation. In this study, the objective was to establish the optimum conditions such as pH, surfactant, silver and thiosulphate concentrations in order to apply the method to synthetic solutions. Experiments were performed using cationic surfactant dodecylamine (DA), as a frother ethanol. High recoveries of silver from aqueous solutions containing thiosulphates and optimum conditions for the recovery of silver were obtained.

Doyle et al. 2003 observed the fundamental characteristics of ion flotation in the context of their implications for commercial applications. These characteristics included the kinetics of metal ion removal, the ability to recover metal values from the foam

product, the ability to separate ions selectively from mixed solutions and a comparison of the performance of ion flotation with other separation methods.

Girek et al. 2004 studied that the competitive ion flotation of Cu^{2+} , Zn^{2+} , Cd^{2+} cations from diluted aqueous solutions. Firstly, they prepared β – cyclodextrin (β -CD) polymer. The chemical structure of the polymers were determined using high performance size exclusion chromatography (HPSEC) with refractive index (RI) detector and H-NMR spectroscopy. They obtained results of ion flotation of copper (II) by using nonylphenol polyoxyethyl glycol ether as an non-ionic surfactant and β -CD polymers as complexation agent, showed the removal of metal decreases with higher molecular mass of β -CD polymers.

Pavloska et al. 2003 examined that selective separation of impurities contained in aragonite (CaCO_3) before their determination by AAS was performed by flotation. Preliminary tests were performed in order to find suitable optimal concentration of aragonite solution for flotation. They found the detection limit of AAS method and determined by electrothermal atomic absorption spectrometry (ETAAS). They proved in this study that flotation could solve very important problems characteristic of ETAAS analysis of trace element in minerals resulting of matrix interferences.

Doyle et al. 2003 reported that the effect of a neutral chelating ligand, triethylenetetraamine (Trien), on the ability to separate copper (II) and calcium (II) ions and compared the ion flotation behaviour of Cu^{2+} and Ni^{2+} aquo-ions with the behaviour of Cu-Trien^{2+} and Ni-Trien^{2+} complexes. In experiments, SDS was used as the collector. They concluded that the copper was removed preferentially, whereas in the absence of Trien, the calcium was removed. Trien was shown markedly increase the removal rates of Cu^{2+} , Ni^{2+} during ion flotation with SDS and lower the steady-state concentration reached. Surface tension measurements confirmed that Trien enhanced the surface activity and adsorption density for SDS-Cu (II) and SDS-Ni (II) solutions.

The removal of Cd (II) using SDS as a collector was studied by Scorzelli et al. 1999. They also studied in the effect of frothers and the surface tension of the initial solutions. Iso-propanol and methylisobutylcarbinol (MIBC) were used as frothers. Characterization of the sublimate by scanning electron microscopy (SEM) were also examined to understand what occurs during ion flotation. Surface tension data and SEM results showed the reduce in floatability which was related to the adsorption of SDS at interface liquid-gas. The best recovery with a dry foam was obtained as 88,2% in the presence of SDS.

The competitive ion flotation of Zn (II) and Cd (II) ions from diluted aqueous solutions by the anionic surfactant (sodium dodecylbenzenesulfonate) in the presence of 4- thioazolidinone derivatives was studied by Kozlowski et al. 2002. The effect of structural evaluation of 4-thioazolidinone derivatives was also discussed. In this study they concluded that the removal of both metals decreased with higher concentration of 4-thiazolidinones derivatives. The removal of metal ions in competitive ion flotation was found to increase with stability for Cd (II) complexes with tautomeric ligands.

Zouboulis et al. 2003 investigated that the removal of zinc and chromium ions from aqueous solutions by application of a two-stage separation process. The first part consisted of the metal ions sorption onto an appropriate sorbent material and successive flotation followed as the second part. The biologically produced surface active agents Surfactin-105 and Lichenysin-A were examined as alternative collectors for flotation methods. The conclusion was drawn from experimental data; biosurfactants effectively removed sorbent material and presented. Both biosurfactants removed chromium ions after sorption studies. Surfactin was proved to be an effective surfactant for the removal of zinc ions after sorption process.

Competitive flotation of zinc and cadmium ions from dilute solutions by side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 ethers in the presence of nonylphenol nonyethylene glycol ether as the non-ionic foaming agent was investigated by Ulewicz et al. 2003. They reported effects of structural modification of PNP-lariat ethers upon the efficiency and selectivity of ion flotation of zinc and cadmium ions. The influence of Li^+ and Na^+ on Cd^{2+} ion flotation removal was also studied. They found the removal of Cd^{2+} increased with increasing of pH values. The efficiency of cadmium flotation decreased with alkali metal cations concentrations increased.

Lazaridis et al. 2004 was investigated the recovery of copper ions from wastewaters. They used three different mechanisms : ion flotation using xanthates, precipitate flotation generating copper hydroxide and sorptive flotation using zeolites as a sorbent material. Ion and sorptive flotation methods were found to be effective for copper removal while the precipitation method failed.

The removal of chromium III by precipitate flotation from dilute aqueous solutions, using SDS as anionic collector and ethanol as a frother was investigated by Medina et al. 2004. The adequate experimental conditions were obtained through precipitate flotation such as SDS and ethanol concentration and gas flow rate. They

studied the results led to a first order model for the removal of chromium III by precipitate flotation.

Matis et al. 2005 examined the removal of two metal ions copper and chromates by applying two flotation techniques : precipitate and adsorbing colloid flotation. They deduced the conclusions that ; collector (SDS) and frother (ethanol) concentrations had no significant effect on copper removal, collector concentration had no effect for chromium removal and comparison of the three flotation techniques (precipitate, sorptive and adsorbing colloid flotation), in a hybrid configuration, revealed that precipitate flotation had the better influence on membrane performance.

A study concerning the kinetics of $\text{Cu}^{2+}_{\text{aq}}$ ions separation by precipitate flotation using alkylamine type (laurylamine) and alkylammonium salt (lauryltrimethylammonium chloride) as cationic collectors and sodium laurylsulphate and sodium oleate as anionic collectors was presented by Stoica et al. 2003. Obtained data were used to verify the classical first order model and three other first-order models, adjusted to the classical model. They found Cu(II) hydroxide species separation using precipitate flotation followed an overall first-order kinetic.

CHAPTER 3

MATERIALS AND METHODS

3.1. Reagents

Sodium dodecyl sulfate (sodium lauryl sulfate) (SDS, 99%) from Sigma and Hexadecyltrimethyl ammoniumbromide from Sigma were used as collectors. A summary of these surfactants with some common characteristics are given in Table 3.1, while their chemical structures are presented in Table 3.2. Ethanol (C₂H₅OH) from Carlo Erba and methyl isobutyl carbinol (MIBC) from Merck were used as frothers. Copper nitrate (Cu(NO₃)₂) from Sigma, zinc nitrate hexahydrate (N₂O₆Zn, 98%) from Aldrich, chromium (III) chloride hexahydrate (CrCl₃.6H₂O, 99%) from Sigma and silver nitrate (AgNO₃) from Carlo Erba were used to prepare working solutions. The solution pH was adjusted using caustic soda (NaOH) and hydrochloric acid (HCl). Double distilled water which was passed through Barnstead Easypure UV- Compact ultrapure water system (18.3 ohm) was used to prepare the stock solutions.

Table 3.1. Selected Properties of the Surfactants Used in This Study

Commercial Name	Hydrophobic Group	Hydrophilic Group	Molecular Weight g/mol	C.M.C. x10 ⁻³ Moles/L
Anionic Surfactant				
Na-Dodecyl Sulfate	Dodecyl	Sulfate	288	8.25 ^a
Cationic Surfactant				
Hexadecyltrimethyl ammoniumbromide	Hexadecyl	Ammonium	364.5	92.0 ^b

a. Mukerjee and Mysels, 1971

b. Czerniawski, 1966

Table 3.2. Structural Formulas of the Surfactants Used in This Study

Sodium Dodecyl Sulfate	Hexadecyltrimethyl ammoniumbromide
$\text{C}_{12}\text{H}_{25}-\text{O}-\overset{\parallel}{\underset{\parallel}{\text{S}}}-\text{O}^- \dots \text{Na}^+$	$\text{CH}_3-\overset{\text{+}}{\underset{\text{ }}{\text{N}}}-\text{C}_{16}\text{H}_{33}-\text{CH}_3$

3.2. Apparatus

- pH- meter ORION 420A
- Ion Flotation Machine
- Surface Tension Measurement Instrument (Krüss, K10 ST)
- Atomic Absorption Spectrometry (AAS) (Perkin Elmer 2280)

3.2.1 Ion Flotation

Ion flotation experiments were conducted in a one liter cell using a Denver type laboratory flotation machine. A schematic view of the flotation machine is given in Figure 3.1. It consists of a cell where the separation takes place and impeller for mixing the pulp and introducing the air. The experimental conditions for the ion flotation tests were listed in Table 3.3. Solutions for ion flotation were prepared in a 1000ml volumetric flask using appropriate amounts of metal ion with double distilled water to make up 1 liter of solution. Then the solution pH was adjusted to a desired value using HCl or NaOH solutions. The solution was stirred for approximately 10 minutes to ensure consistent mixing of reagents. The solution was then placed in the flotation cell. Firstly, SDS solution was added in certain molar concentration values and mixed with the solution that was in the flotation cell for a time period of 2 minutes. Appropriate amounts of ethanol were added after applying SDS to the solution for 2 minutes. During mixing of SDS, metal ion and ethanol solutions air was flowed through the sparger. Foam samples were taken at preset time intervals as 2, 4, 8 and 16 minutes. The froth products from various time increments were analyzed by atomic absorption spectrometry (AAS) to determine the amount of metal ions that floated. After the experiments the flotation cell was cleaned using 1M HNO₃, with double distilled water.

Table 3.3. Experimental Conditions for the Ion Flotation Tests

Machine Type	Denver Equipment Co.
Volume	1 liter
Rotor Speed	750 rpm
Air Flow Rate	50 ml/min.
Collector	Sodium Dodecyl Sulfate or Hexadecyl trimethyl ammoniumbromide
Frother	Ethanol or MIBC
pH	From 4 to 12
Froth Removal Times	2, 4, 8 and 16 minutes

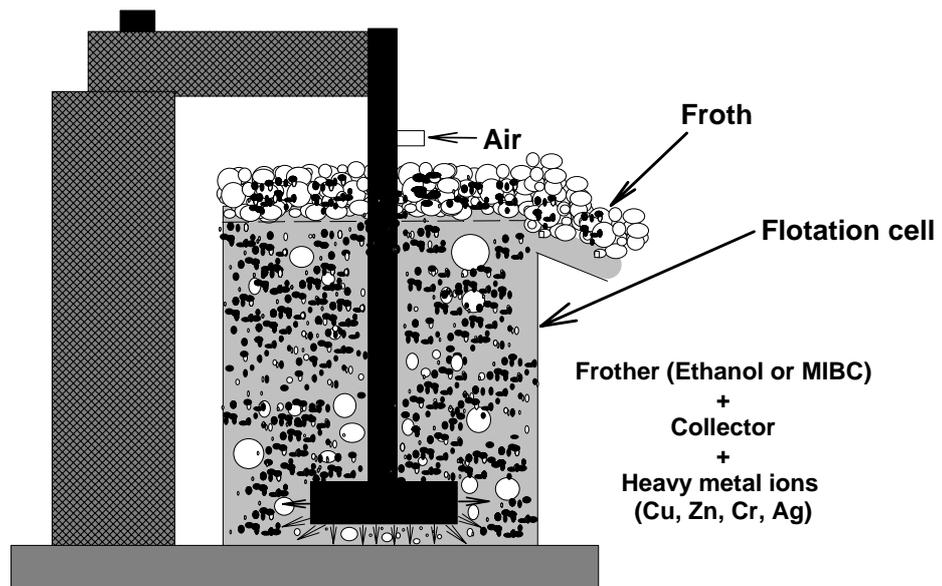


Figure 3.1. A schematic view of the Flotation Machine

3.2.2. Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) uses the absorption of radiation by free gaseous atoms in order to achieve quantitative determination of elements (Welz and Sperling, 1998). An atomic absorption spectrometer measures the absorbance which is the logarithm of the rate of incident light power (P_0) to transmitted light power (P) :

$$A = \text{Log } P_0 / P \quad (3.1)$$

There is a relationship between P_0 and P when a light beam is decreased by the medium through which it passes:

$$P = P_0 \exp(-kL) \quad (3.2)$$

Where k : absorption coefficient which is a function of wavelength of light, number of atoms in the ground state per unit volume.

L : path length in medium

There are two main components in an atomic absorption spectrometer: atom cell which creates atoms at the free gaseous ground state, and optical system to measure the signal. Atom cell dissolves the liquid sample and dissociates analyte elements into their free gaseous ground state form in which the atoms are available to absorb radiation coming from light source and to create a measurable signal which is proportional to concentration (Tyson and Haswell 1991). The atomizer, in which the analyte is atomized, is flame, graphite tube or quartz tube. In flame atomization fixed aliquot of measurement solution is converted into an aerosol in nebulizer and transported into the flame which must have enough energy both vaporize and atomize the sample (Welz and Sperling 1998).

3.2.3. Surface Tension Measurements

The surface tension of SDS solutions were measured at 25 °C with a Krüss K10 ST model using the ring type surface tension method. All glassware for the measurements was thoroughly cleaned using concentrated nitric acid solution and rinsed with double distilled water. Between measurements, the ring was rinsed many times in double distilled water and then burned in a flame. Different concentrations of SDS solutions from 10^{-2} M to 10^{-6} M were prepared. Then a fixed amount of sample (35 ml) was taken for the measurement in each case. Before the sample was taken it was mixed

for 1 minute and all samples were made to wait for 2 minutes to obtain stability. Each surface tension value presented here was the averaged value of three measurements.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Surfactants

The role of surfactant molecules in ion flotation is significant which was discussed in Chapter II. The forms of surfactant molecules in aqueous system change with their concentrations. In order to study these changes surface tension measurements were done as a function of SDS concentration and the results were discussed in the following paragraphs.

Surface Tension

The surface tensions of the aqueous SDS solutions were measured and the results were presented in Figure 4.1 as surface tension (γ) versus concentration (Conc.) curves. It is seen that there are three regions and two breaks in the curve. The second break at around 8×10^{-3} mol/ L is so distinct that the surface tension values level off and show a nearly constant value after this concentration (Region III). This is the critical micelle concentration (CMC) which is the concentration at which the single molecules come together to form aggregates known as micelles. In region I and II where the concentrations less than CMC, however surfactant molecules are in their single form and contributes to the decrease in surface tension. In region II, however, the slope of the curve is constant, meaning that the surface has reached a monolayer coverage. Surface tension, however continues to decrease due to exchange between the bulk molecules and the surface molecules constantly and increase in the rate of this process with an increase in concentration.

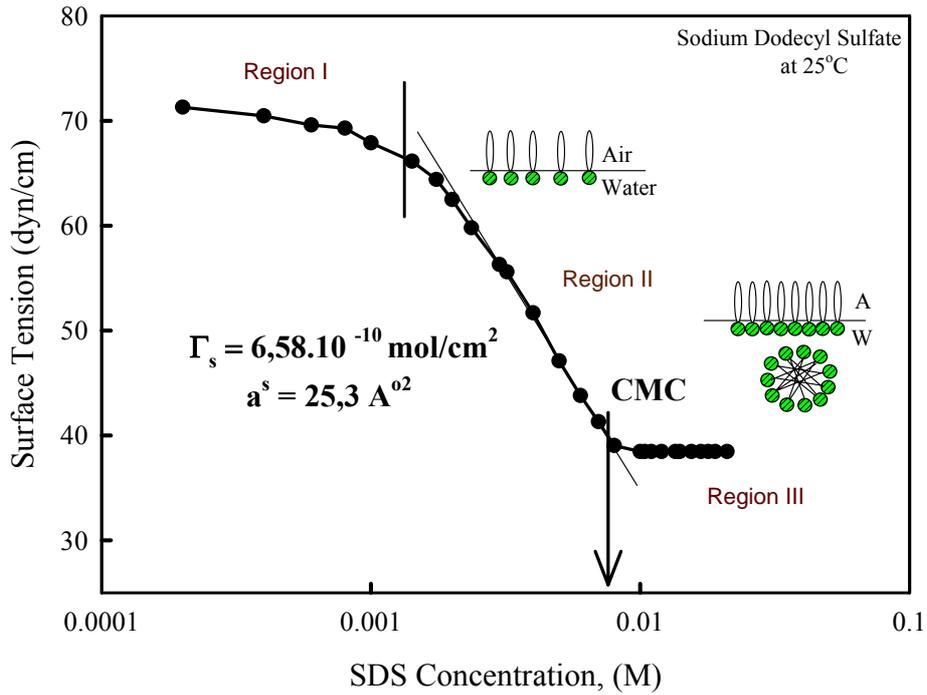


Figure 4.1. Surface Tension of SDS solution at 25 °C

The slope of this curve could be used to calculate the adsorption of surfactant molecules at air/water interface using Gibb's adsorption equation. The most general form of Gibbs adsorption equation,

$$d\gamma = -\sum \Gamma d\mu \quad (4.1)$$

where $d\gamma$: the change in surface tension of the solvent,

Γ : the surface excess concentration of any component of the system,

$d\mu$: the change in chemical potential of any component of the system,

is fundamental to all adsorption processes (Rosen 1989).

For dilute solutions (10^{-2} M or less) which contain only one nondissociating surface active solute, the activity of the solvent and the activity coefficient of the solute can be considered to be constant. Thus,

$$d\gamma = -RT \Gamma d\ln C \quad (4.2)$$

$$d\gamma = -2.303 RT \Gamma d\log C \quad (4.3)$$

which is the formula in which the Gibbs equation is commonly used for solutions of surfactants.

When γ is in mN/m (equal to mJ/m^2) and $R = 8.31 \text{ J/mol K}$, then Γ is in $\text{mol}/1000\text{m}^2$. From the surface excess concentration, the area per molecule at the interface a^s , in square angstroms ($\text{A}^{\text{o}2}$) is calculated from the relation.

$$a^s = 10^{16} / N \Gamma \quad (4.4)$$

where N : Avogadro's number and Γ is in mol/cm^2 .

The surface excess concentration (Γ) was calculated by using equation (4.3) and found $6.58 \cdot 10^{-10} \text{ mol}/\text{cm}^2$. Applying this value in equation (4.4) the area per molecule at the interface (a^s) was obtained as $25.3 \text{ A}^{\text{o}2}$ per SDS molecule. This value could be helpfull to imagine in comparing the sizes of the surfactant heads and the ions.

4.2. Frothers

Frothers in ion flotation play very important role due to their effect on bubble formation. They adsorp at air/water interface and influence surface tension. This effect was studied and the results were presented in Figure 4.2. It is seen that the effect of a frother on surface tension changes as a function of its concentration and the presence of other species (such as surfactants and metal ions) in the system. And also seen that in the case of increasing concentrations of MIBC, surface tension decreased sharply compared to increasing ethanol concentrations. This might be due to the number of carbon atoms that found in the structure of MIBC and ethanol (MIBC has six, ethanol has two carbon atoms in their structure).

The effect of ethanol on surface tension was small when also a surfactant is present in the system. This might be due to the availibility of ethanol for surface to decrease surface tension. That is it is not available for surface when surfactant molecules are present. However, the presence of metal ions decreased their influence on the ethanol action. Figure 4.4 gives these results for different metal ions. The varying effects of metals on the action of ethanol to decrease surface tension shows the varying affinities of metal ions on surfactant molecules. If a metal ion has more affinity to surfactant, it will attach to it and decrease its effect on the action of ethanol. Ethanol will be free to adsorp at interface and decrease surface tension at the concentrations used in this study (Figure 4.3.).

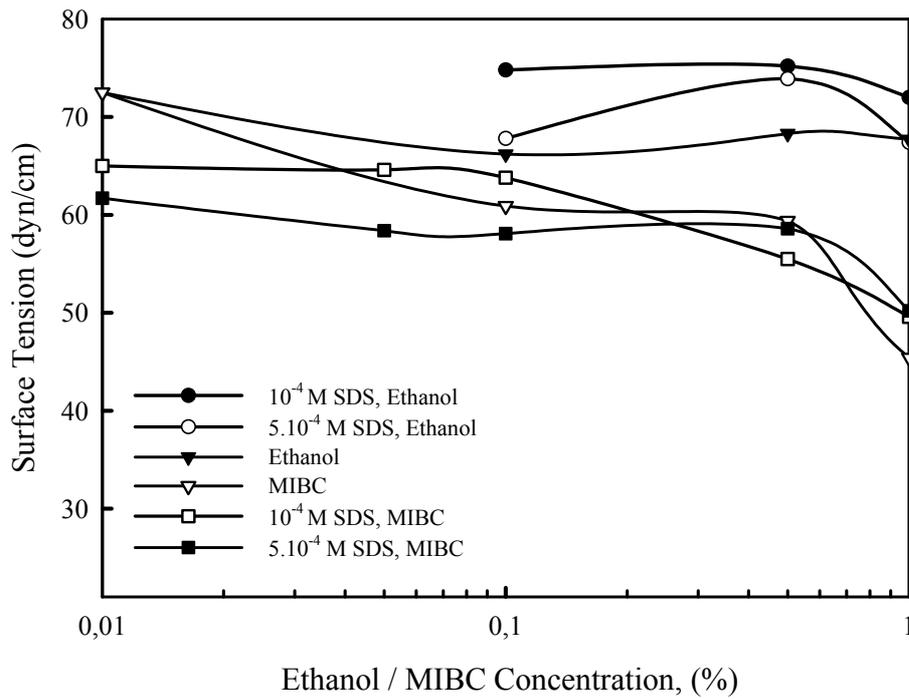


Figure 4.2. Surface Tension of Ethanol / MIBC and SDS Solution.

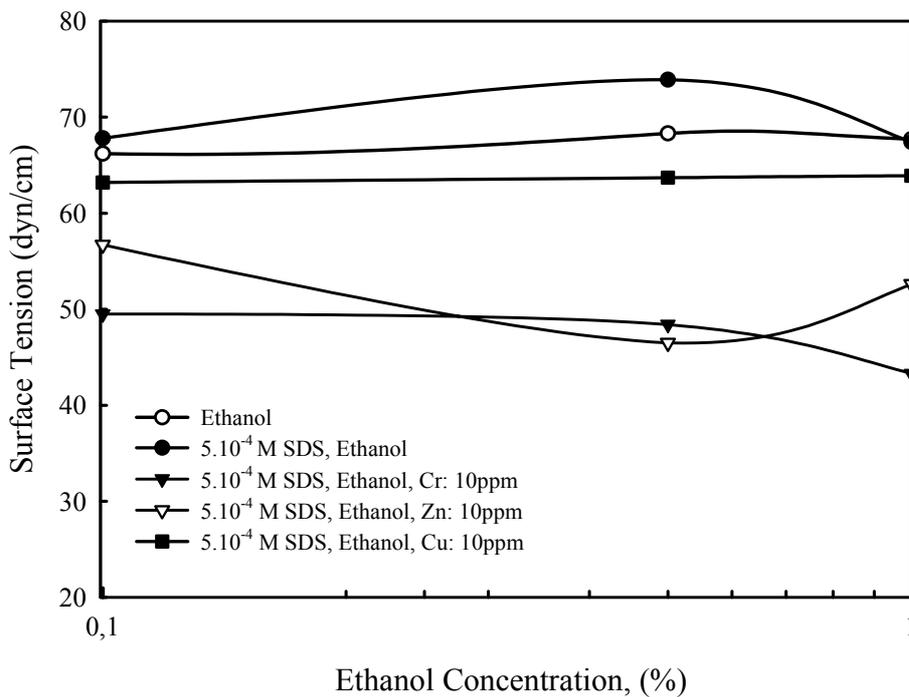


Figure 4.3. Surface Tension of Ethanol / MIBC and SDS Solution with Metals.

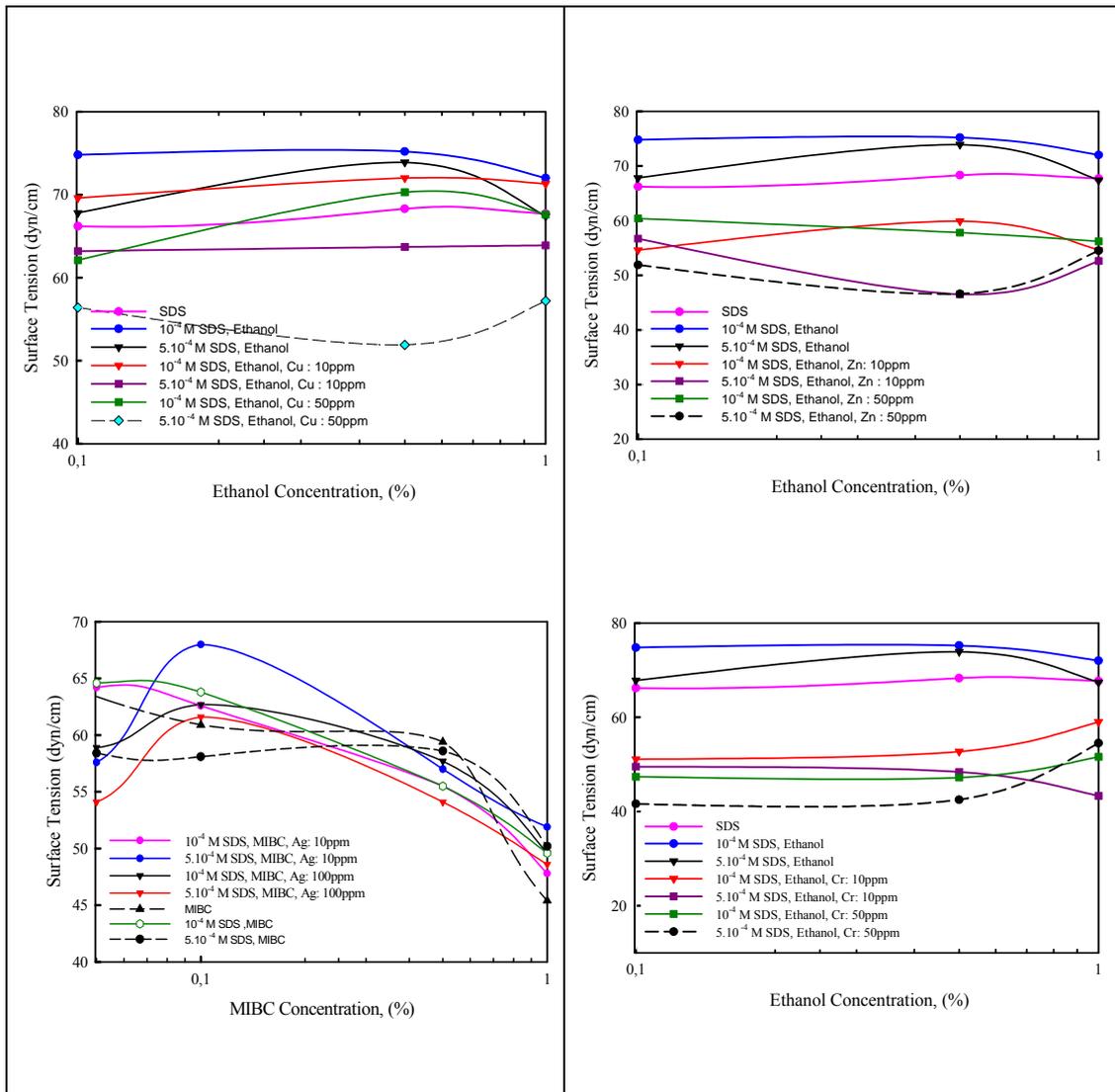


Figure 4.4. The Effect of Ethanol / MIBC Solution and Their Mixture of SDS with / without Different Concentrations of Metals on Surface tension.

4.3. Metals

4.3.1. Forms of Metal Ions in Water as a Function of pH

pH is a significant factor for determining the form of the metallic species. Because pH of the solution influences the distribution of the various species. When determining various metal species equilibrium models for many metals are constructed using the set of equations used for simple acid-base calculations. First, total concentrations of all components are stated; then all possible species are identified; and mass balances, a charge balance and equilibrium equations are written. However, it is time wasting to solve these equations manually. Because of this, computer solution was needed. Instead of this way, Visual Minteq ver.2.15 was used. After obtaining the form of the metallic species, graphs were drawn for copper, zinc, silver and chromium concentrations as a function of pH and given in Figures 4.5, 4.6, 4.7, 4.8. The pH is one of the principal factors influencing the separation of ions by flotation, as it determines the magnitude and sign of the charge on ions. This makes one to decide which surfactant to use in flotation.

Figure 4.5 gives the distribution of copper species as a function of pH for 10ppm concentration. It is seen that there are negatively and positively charged Cu species between pH: 4 and 12. For pH values between 4 and 11, copper and its species are positively charged, however, for pH values higher than 11 they are negatively charged. As a result, knowing the type of species present in the solution will help one to decide the most suitable surfactant, anionic or cationic, to use.

Figure 4.6 gives the distribution of zinc species as a function of pH for 10ppm concentration. In case of low pH values ($< \text{pH } 5$), positively charged zinc (II) species are dominant. In case of high pH values (pH 5-12), however, there are several zinc species with different charges.

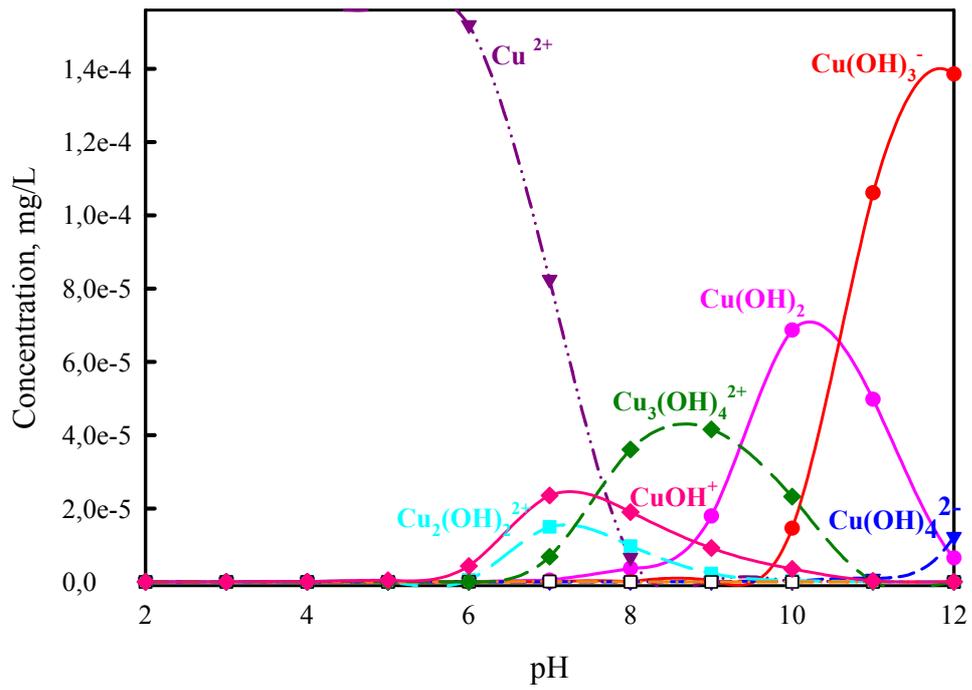


Figure 4.5. Forms of Copper (10 mg/L) in Water as a Function of pH

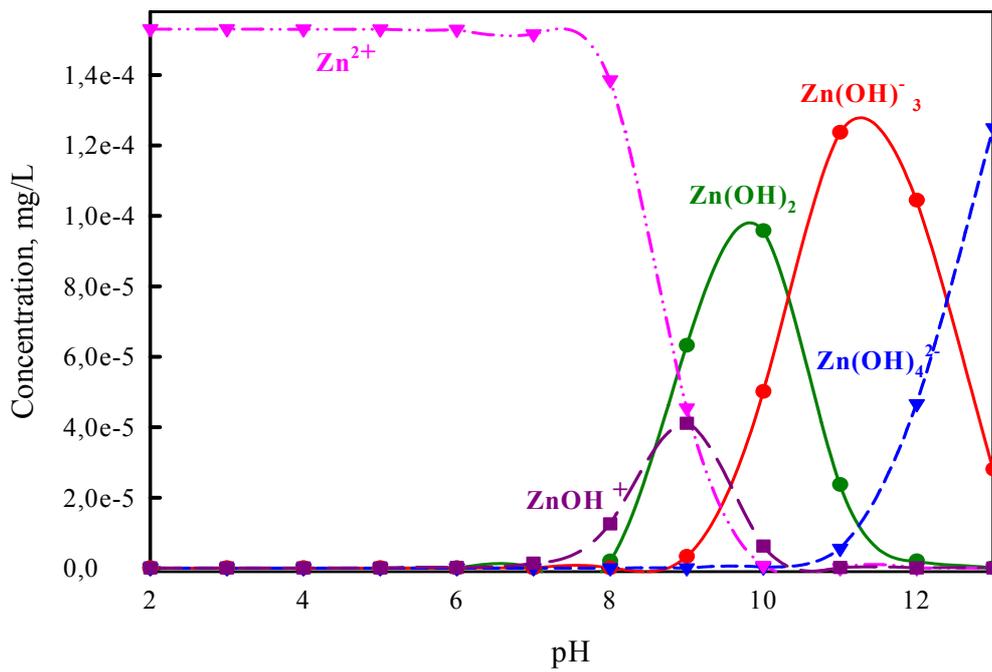


Figure 4.6. Forms of Zinc (10 mg/L) in Water as a Function of pH

Figure 4.7 gives the distribution of silver species as a function of pH for 10mg/L concentration. According to this Figure, there are negatively charged silver species for pH values from 10 to 12. At low pH values, positively charged silver species are dominant.

Figure 4.8 gives the distribution of chromium species as a function of pH for 10mg/L concentration. In low values, the main aqueous Cr (III) species are Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$ and $\text{Cr}(\text{OH})_3^+$. Cr^{3+} species are seen only at a pH values lower than 4. When the pH value is higher than 10, the species with negative charge becomes dominant.

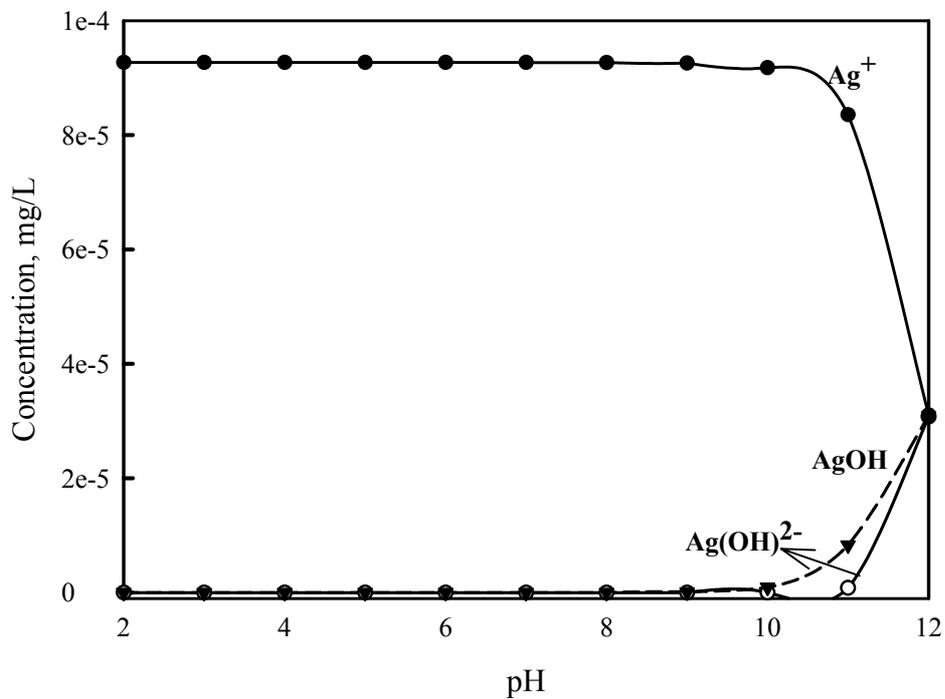


Figure 4.7. Forms of Silver (10 mg/L) in Water as a Function of pH

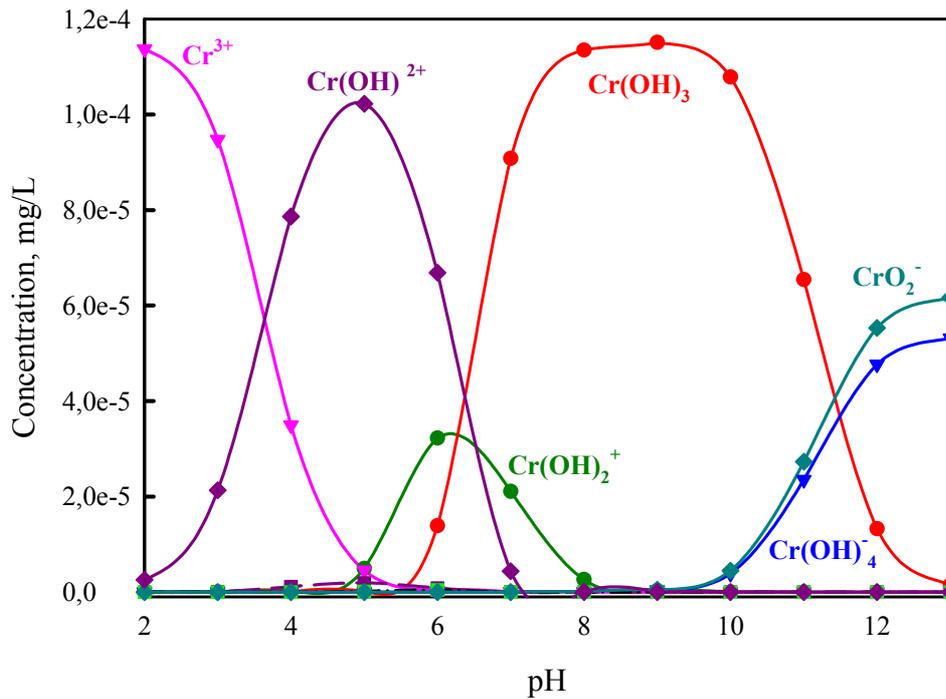


Figure 4.8. Forms of Chromium (10 mg/L) in Water as a Function of pH

Forms of metal ions in water in case of higher concentrations as a function of pH were represented in Appendix B. Increasing total copper, zinc, silver and chromium concentrations influence the metal species, their concentrations in water and their sign of the charge at the given pH value.

4.4. Ion Flotation Studies

Flotation experiments were carried out as a function of time (2, 4, 8, 16 minutes) and metal (Cu, Zn, Ag, Cr) recoveries were calculated using the procedure given in Chapter III. Sodium dodecyl sulfate / hexadecyl trimethyl ammoniumbromide and ethanol/ methylisobutyl carbinol were used as collectors and frothers respectively. 50 ml/min was selected as a flowrate. The results were presented in following paragraphs for each metal ion.

4.4.1. Copper

The results of copper were presented in Figures 4.9 and 4.10 for different ethanol concentrations as 0.1%, 0.5% and 1% for each surfactant concentration of 10^{-4} M, 5×10^{-4} M and 10^{-3} M. These results were also presented as a tridimensional plot in Figure 4.11 to look at the picture differently. SDS was used as an anionic surfactant at the pH used (pH 4) due to positive charge of the ionic species present (see also Figure 4.5). At 10^{-4} M of SDS, the copper recovery was very low. The change in ethanol concentration did not make any difference in this result. At 5×10^{-4} M SDS, the copper recoveries were 59%, 74% and 51% for 0.1, 0.5, and 1.0% of ethanol concentrations respectively. At 10^{-3} M SDS, the copper recoveries were 44%, 70%, 52% for 0.1, 0.5, and 1.0% of ethanol concentrations, respectively. As it is seen from Figure 4.11 that at low concentrations of surfactant changing ethanol concentration did not make any difference where there is no collector metal ion attachment. At higher concentrations, however, the recoveries changed with ethanol concentration and an optimum was observed around 0.5%.

When ethanol concentrations were 0.1% and 1%, the production of foam was affected and stopped after 16 minutes. However, it continued up to 32 minutes in case of 0.5% case. This results was explained by Duyvesteyn (1994) as follows. According to these investigators, at low concentrations of alcohol, the metal-collector complex may be stabilized by alcohol molecules through “ hydrophobic interaction ” with the hydrocarbons chains of the frother. The detrimental action of higher concentrations of alcohol may be due to fact that the metal- collector complexes are stabilized so well in the aqueous solution that they are less likely to adsorb at the air-interface. Also at the higher alcohol concentrations, the number of sites on the interface liquid-gas available for metal-collector complex adsorption will be reduced due to adsorption of alcohol molecules, which may lower metal removal.

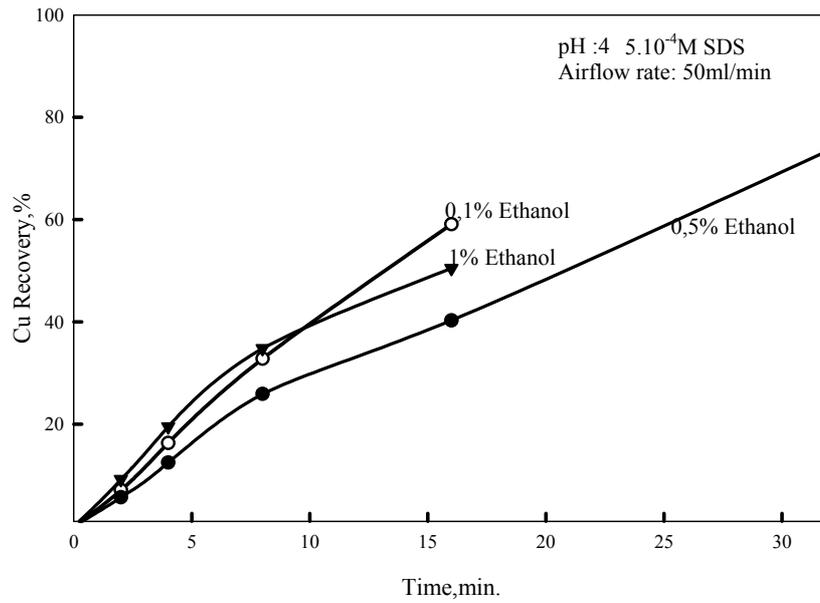


Figure 4.9. Effect of Ethanol Concentration on Copper Recovery as a Function of Time. (Initial copper concentration: 10 mg/L; SDS concentration : 5.10^{-4} M; pH: 4; Airflow rate: 50ml/min.)

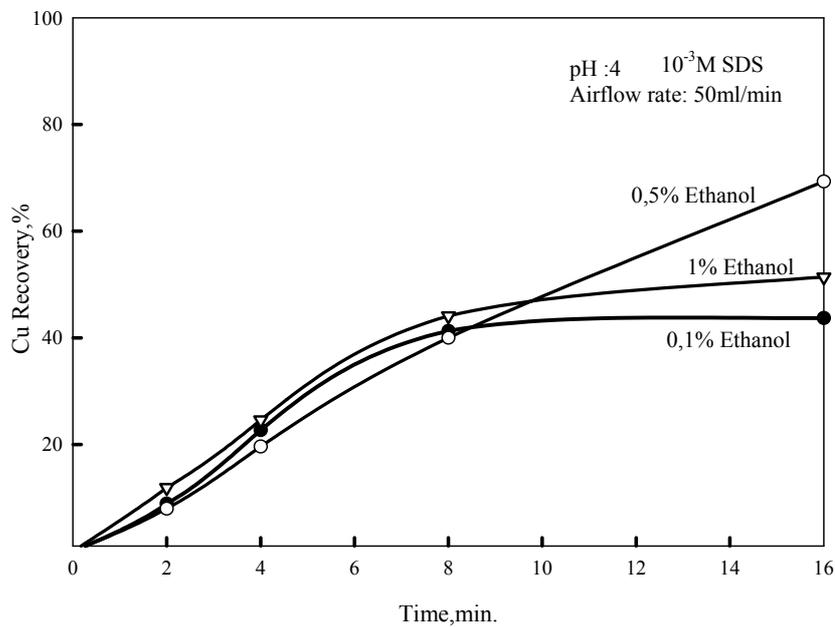


Figure 4.10. Effect of Ethanol Concentration on Copper Recovery as a Function of Time. (Initial copper concentration: 10 mg/L; SDS concentration : 10^{-3} M; pH: 4; Airflow rate: 50ml/min.)

Different air flowrate values of 50, 150, 250 ml/min were also tested for $5 \cdot 10^{-4}$ M SDS, pH: 4 and 0.5% of ethanol condition. It is seen from the Figure 4.12 that 250 ml/min. gave the maximum recovery but the amount of foam produced was so high.

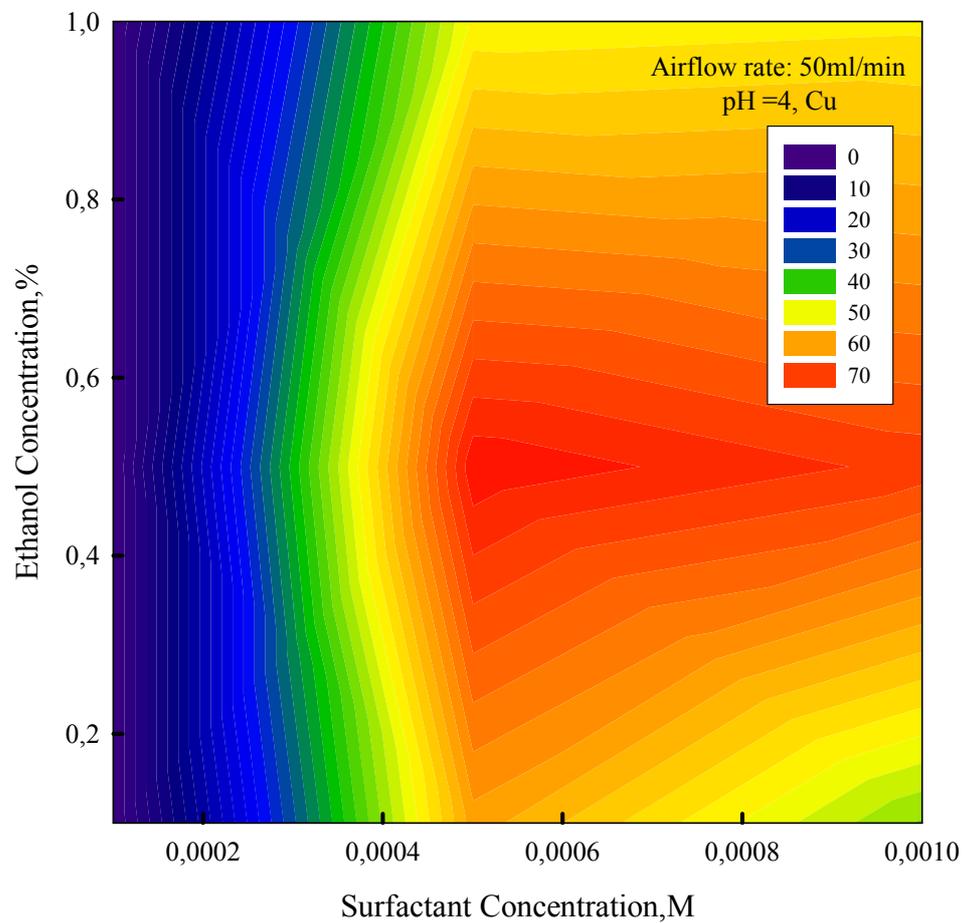


Figure 4.11. Effect of Ethanol Concentration and Surfactant Concentration on Copper Recovery as a Function of Time. (Initial copper concentration: 10 mg/L; Airflow rate : 50 ml/min.; pH: 4)

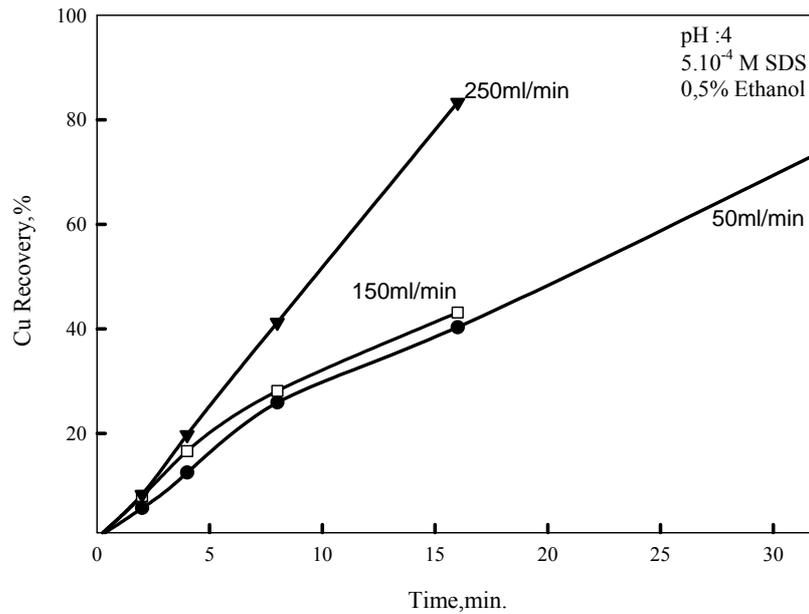


Figure 4.12. Effect of Airflow rate on Copper Recovery as a Function of Time. (Initial copper concentration: 10 mg/L; SDS concentration : 5.10^{-4} M; pH: 4; Ethanol: 0.5%.)

The copper recoveries were also plotted as a function of the water recoveries and presented in Figures 4.13 and 4.14. This kind of analyzing has not coincided in literature yet. These type of plotting helps one to have also an idea about the amount of water collected during separation. Scorzelli and Fragomeni et. al, 1999, discussed in the large volume of foam but their results did not show the recovery exactly. Scorzelli et al. 1999, Lazaridis et al. 2004, Matis et al. 2005, Girek et al. 2004, Kozłowski et al. 2002, Charewicz et al. 1999, determined the recovery of metals as a function of time but did mention water recovery.

In Figure 4.13, the crossed line which is from one corner to another is 50 – 50 split line. This means no separation occurs at that condition. If the flotation results approach to the axis of y, it means metal concentration is in the froth phase but if the results approach to the axis of x, it is understand that metal concentration is in the flotation cell. The analyzing the results this way also showed that the highest recovery was at 0.5% ethanol and 5.10^{-4} M SDS concentrations at pH 4.

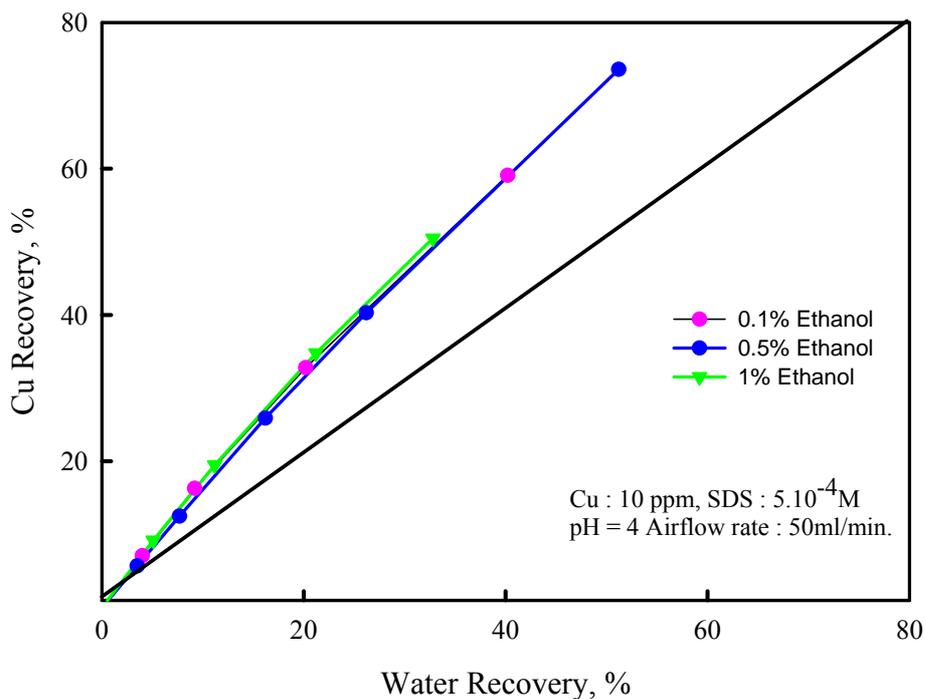


Figure 4.13. Copper Recovery as a Function of Water Recovery. (Initial copper concentration: 10 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 5.10^{-4} M)

When the initial copper concentration was increased to 50 mg/L in the presence of 5.10^{-4} M SDS and 0.5 % ethanol at pH 4 , the recovery decreased to 42%. This might be due to the higher number of copper ions compared to the surfactant molecules present. The number of copper ions is equal to 9.48×10^{19} and 47.25×10^{20} in case of 10 mg/L and 50 mg/L respectively. The number of surfactant molecules, on the other hand did not changed and stayed as 30.1×10^{19} which may not be enough for 50 mg/L copper concentration. This also supports the mechanism proposed for ion flotation discussed in Chapter II. That is metal ions attach to surfactant molecules with opposite charge on them and therefore attach to the air bubble and floats (see also Figure 2.2a and b).

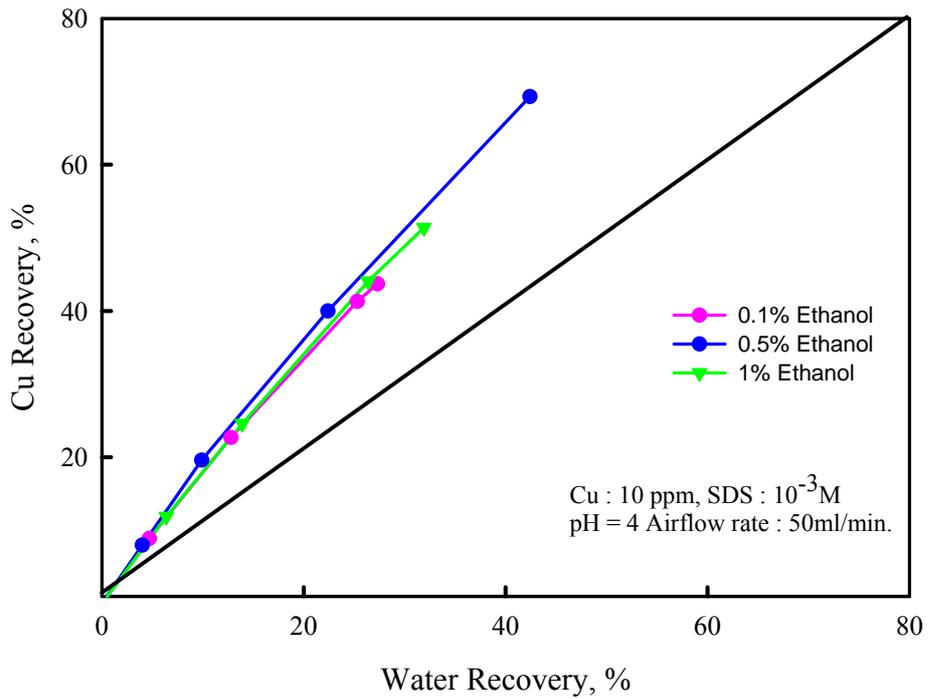


Figure 4.14. Copper Recovery as a Function of Water Recovery. (Initial copper concentration: 10 mg/L; Airflow rate : 50 ml/min.; pH: 4, SDS : 10^{-3} M)

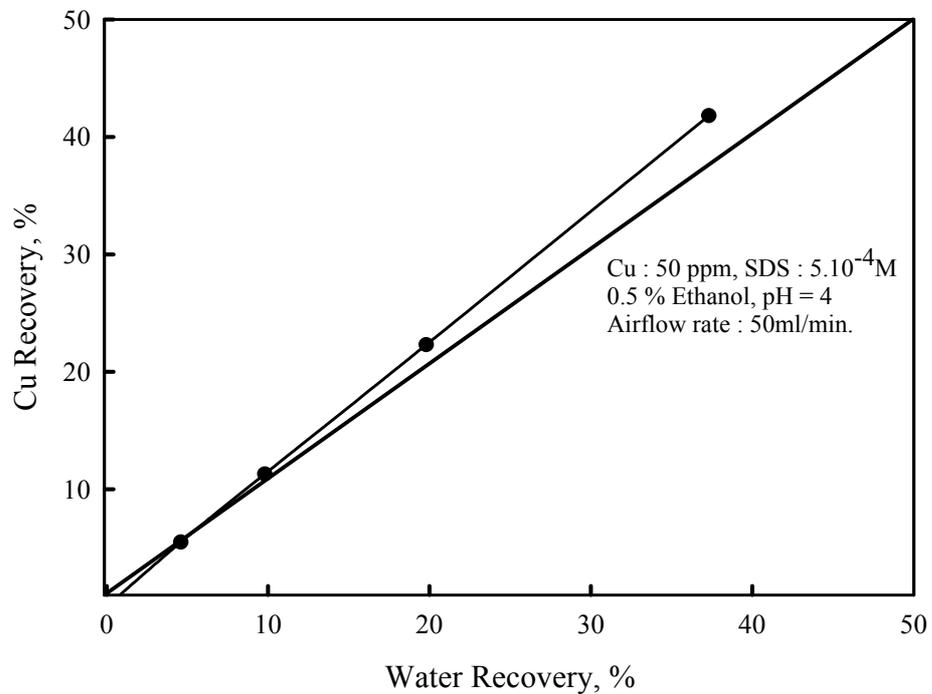


Figure 4.15. Copper Recovery as a Function of Water Recovery. (Initial copper concentration: 50 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 5.10^{-4} M)

4.4.2. Zinc

The results of zinc were presented in Figures 4.17 and 4.18 for different ethanol concentrations as 0.1%, 0.5% and 1% for each surfactant concentration of 10^{-4} M, $5 \cdot 10^{-4}$ M and 10^{-3} M. These results were also presented as a tridimensional plot in Figure 4.16 to see the picture clearly. SDS was used as an anionic surfactant at the pH value of 4 due to charge of the ionic species present (in Figure 4.6). The zinc recovery, at 10^{-4} M of SDS, was so low. At $5 \cdot 10^{-4}$ M SDS, the zinc recoveries for 0.1, 0.5, and 1.0% of ethanol concentrations were 69%, 62% and 58% respectively. At 10^{-3} M SDS, the zinc recoveries for 0.1, 0.5, and 1.0% of ethanol concentrations were 67%, 63%, 55%, respectively. As it is seen from Figure 4.16 that at higher concentrations of surfactant, the recoveries changed with ethanol concentration and an optimum was observed around 0.1%.

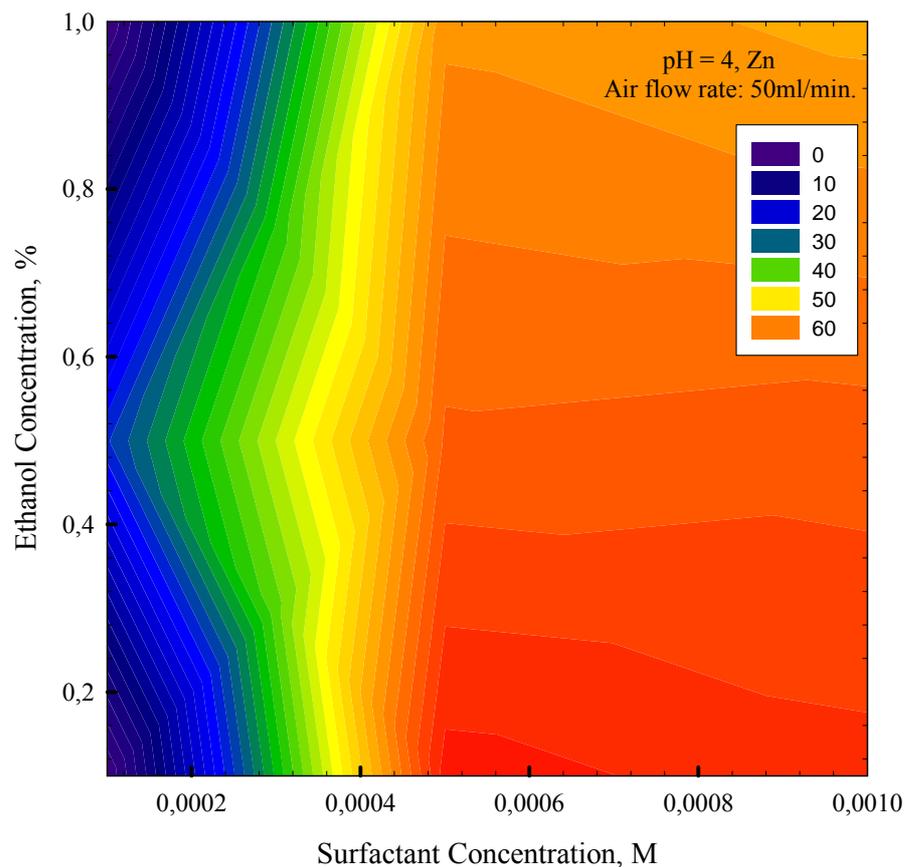


Figure 4.16. Effect of Ethanol Concentration and Surfactant Concentration on Zinc Recovery as a Function of Time. (Initial zinc concentration: 10 mg/L; pH: 4)

The recoveries of zinc were also drawn as a function of the water recoveries and presented in Figures 4.17 and 4.18. The results also showed that the highest recovery (69%) was at 0.1% ethanol and 5.10^{-4} M SDS concentrations at pH 4.

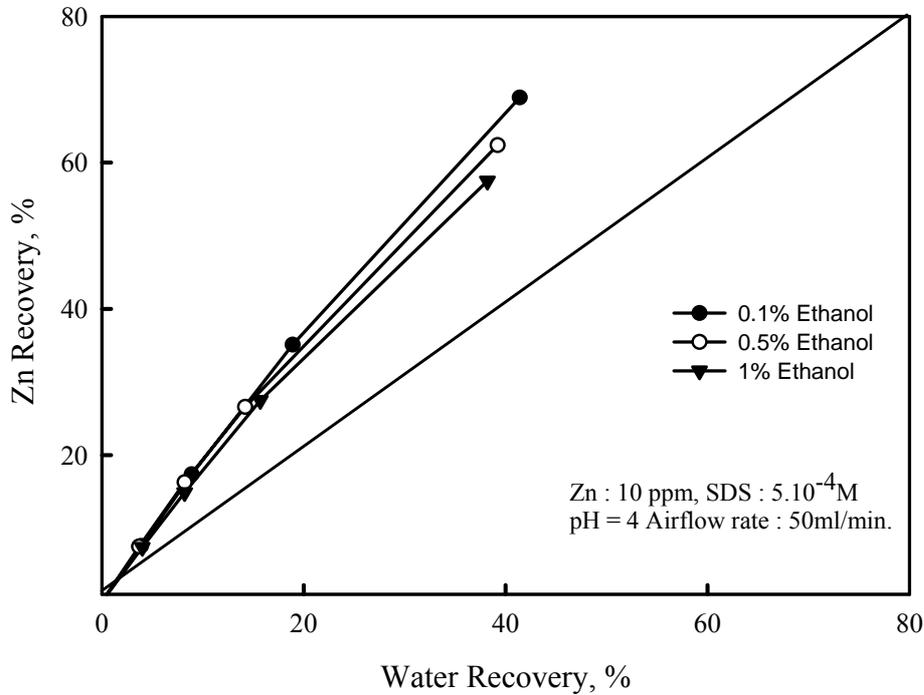


Figure 4.17. Zinc Recovery as a Function of Water Recovery. (Initial Zinc concentration: 10 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 5.10^{-4} M)

In Figure 4.19, the initial zinc concentration was increased to 50 ppm in the presence of 5.10^{-4} M SDS and 0.1 % ethanol at pH 4 , the recovery decreased to 41%. It might be because of the high number of zinc ions compared to the surfactant molecules present. The number of zinc ions is equal to 9.21×10^{19} and 4.60×10^{20} in case of 10 mg/L and 50 mg/L respectively. The number of surfactant molecules, on the other hand did not changed and stayed as 30.1×10^{19} which is not enough for 50 mg/L zinc concentration.

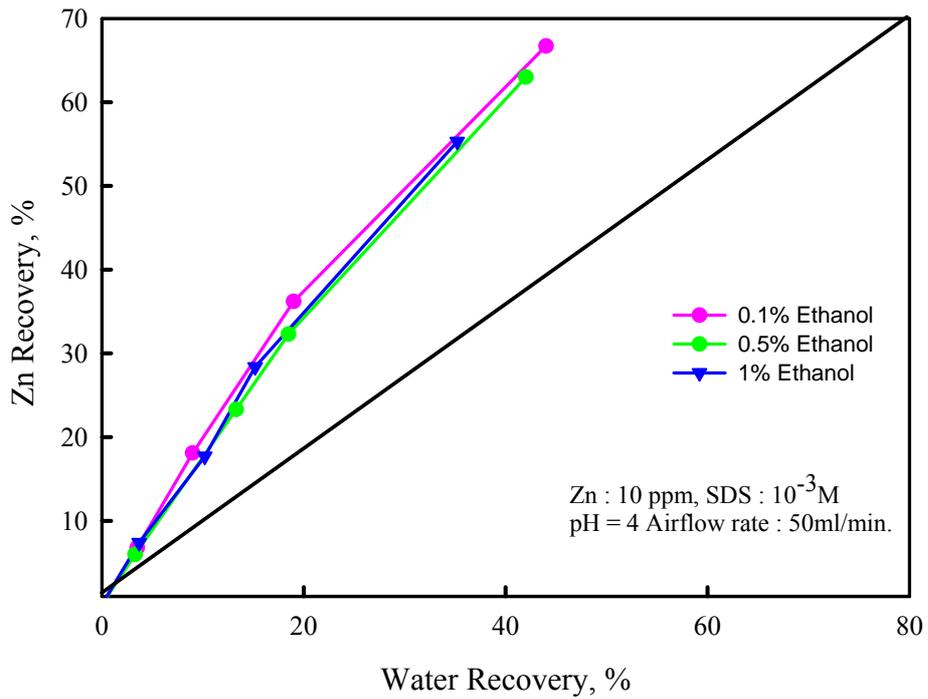


Figure 4.18. Zinc Recovery as a Function of Water Recovery. (Initial Zinc concentration: 10 mg/L; Airflow rate : 50 ml/min.; pH: 4, SDS : 10^{-3} M)

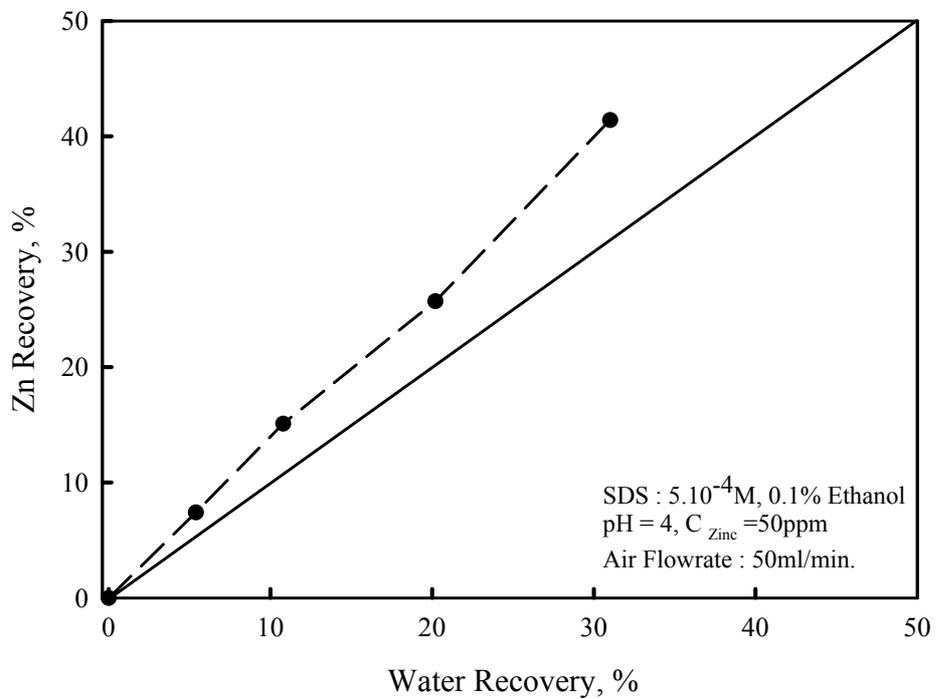


Figure 4.19. Zinc Recovery as a Function of Water Recovery. (Initial zinc concentration: 50 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 5.10^{-4} M)

4.4.3. Silver

In the flotation studies of silver, firstly, ethanol was used as a frother, but the presence of different ethanol concentrations did not influence the silver recovery apparently in the whole pH range. Because of this case, another type of frother as known as methyl isobutyl carbinol (MIBC) was used in the experiments of silver. For the selected MIBC concentrations, 0.01%, 0.05% and 0.1% for each surfactant concentration of 10^{-4} M, 5.10^{-4} M and 10^{-3} M were performed and presented in Figure 4.20 as a tridimensional plot. At 10^{-4} M SDS, the silver recoveries for 0.01, 0.05, and 0.1% of MIBC concentrations were 50%, 47% and 73% respectively. At 5×10^{-4} M SDS, the silver recoveries for 0.01, 0.05, and 0.1% of MIBC concentrations were 49%, 53%, 45%, and at 10^{-3} M SDS, recoveries of silver were 47%, 50% and 39% respectively. These results are seen in Figures 4.21, 4.22 and 4.23 clearly. As it is seen from Figure 4.20 that at higher concentrations of surfactant, the recoveries did not change with MIBC concentration and an optimum was observed around 0.1%.

For the tests using a higher concentration of collector (10^{-3} M), a greater amount of foam was formed, causing the decrease in the removal of silver flotation. According to Pinfold (1972), the decrease of the species removal for increasing collector concentrations can be due to competition between coligend-collector complex and free ion collectors for a place in the surface of the bubble.

In Figure 4.24, silver concentration was increased to 100 ppm in the presence of 10^{-4} M SDS and 0.1 % MIBC at pH 4, the recovery decreased to 41%. It might be because of the high number of silver ions compared to the surfactant molecules present. The number of silver ions is equal to 5.58×10^{19} and 5.58×10^{20} in case of 10 mg/L and 100 mg/L respectively. The number of surfactant molecules, on the other hand did not change and stayed as 30.1×10^{19} which is not enough for 100 mg/L silver concentration.

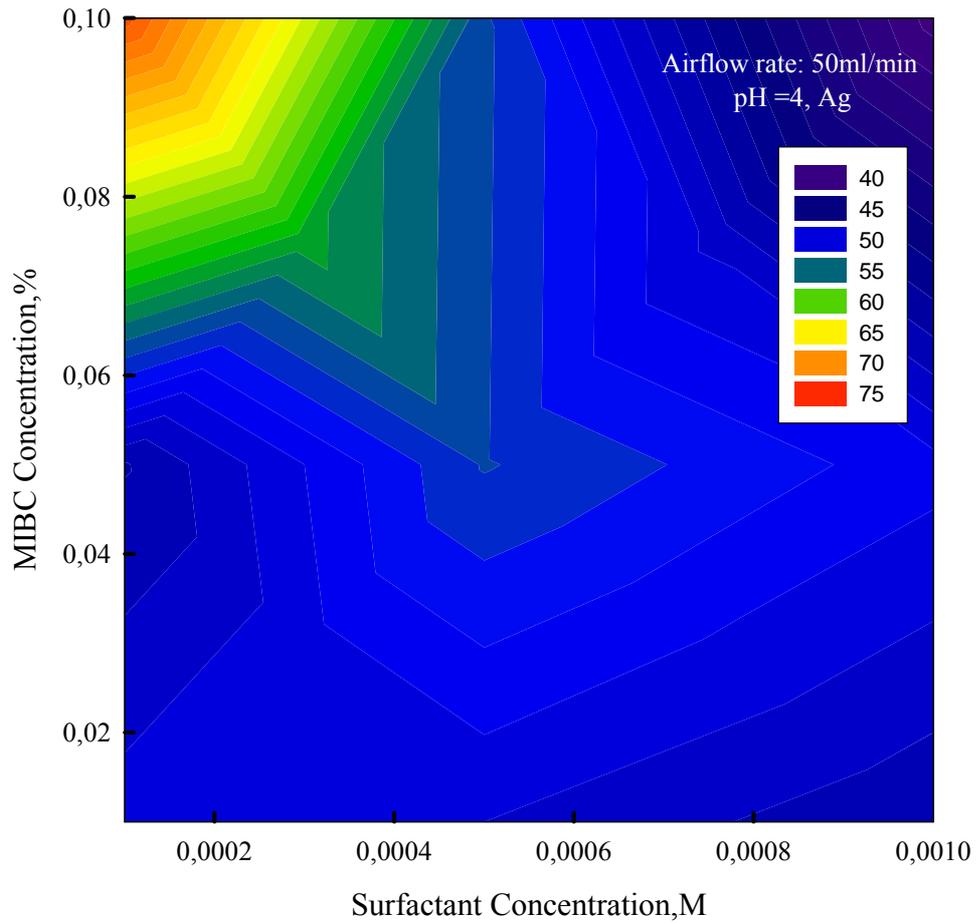


Figure 4.20. Effect of MIBC Concentration and Surfactant Concentration on Silver Recovery as a Function of Time. (Initial silver concentration: 10 mg/L; Airflow rate : 50 ml/min.; pH: 4)

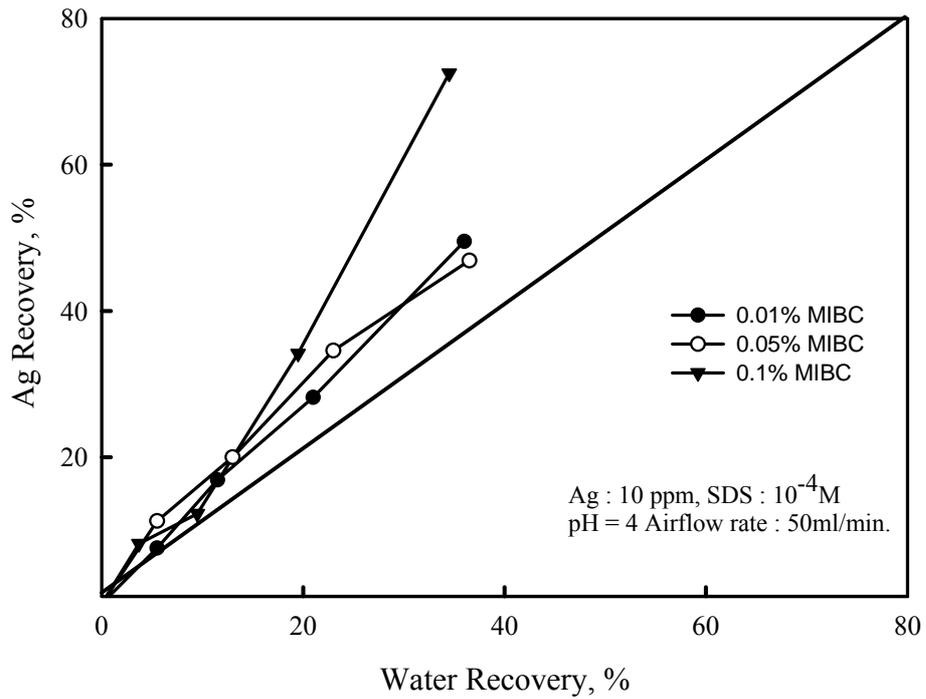


Figure 4.21. Silver Recovery as a Function of Water Recovery. (Initial Silver Concentration: 10 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 10^{-4} M)

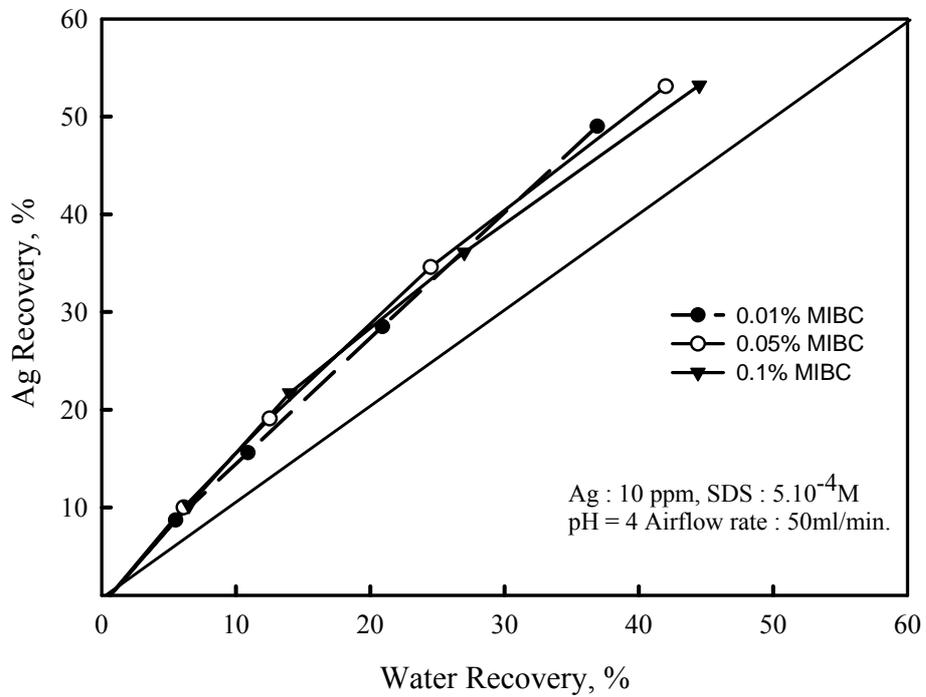


Figure 4.22. Silver Recovery as a Function of Water Recovery. (Initial Silver Concentration: 10 mg/L, pH: 4, SDS: 5.10^{-4} M)

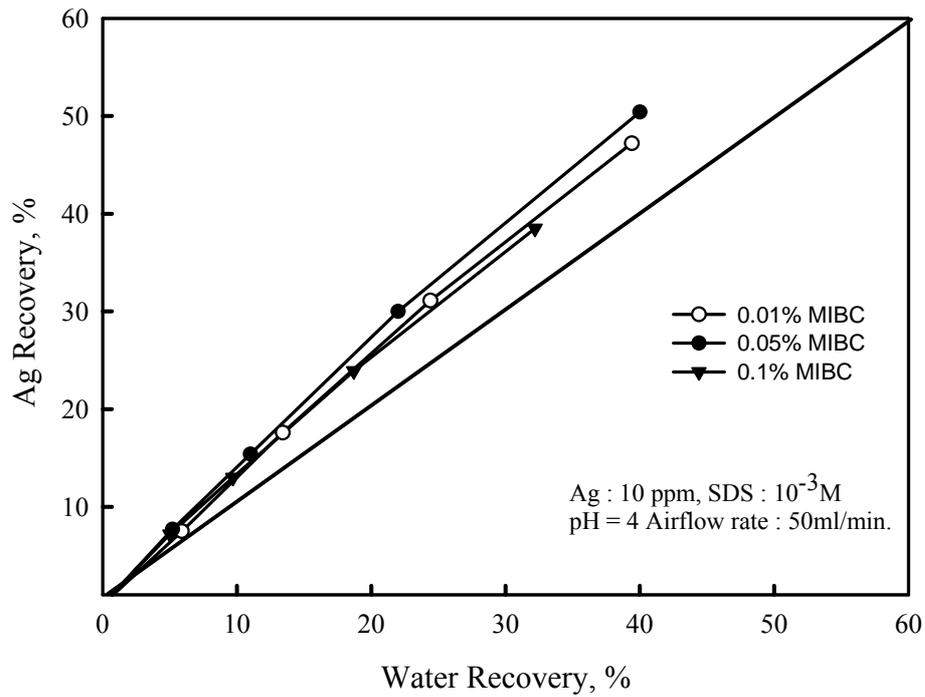


Figure 4.23. Silver Recovery as a Function of Water Recovery. (Initial Silver Concentration: 10 mg/L; Airflow rate: 50 ml/min.; pH: 4, SDS: 10^{-3} M)

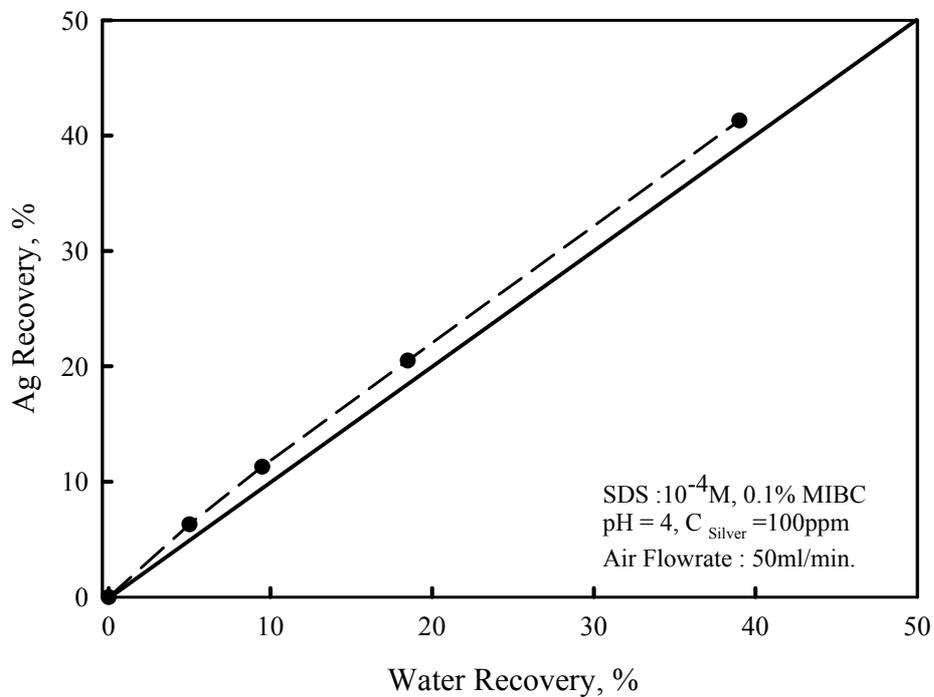


Figure 4.24. Silver Recovery as a Function of Water Recovery. (Initial silver concentration: 100 mg/L; pH: 4, SDS : 10^{-4} M)

4.4.4. Chromium

The results given in Figures 4.25 and 4.26 show the effect of different ethanol concentrations as 0.1%, 0.5% and 1% and SDS concentration of 10^{-4} M, $5 \cdot 10^{-4}$ M and 10^{-3} M on flotability of chromium (III). The recoveries of chromium, at 10^{-4} M of SDS, were low. The chromium recoveries for 0.1, 0.5, and 1.0% of ethanol concentrations at $5 \cdot 10^{-4}$ M SDS, were 40%, 40% and 46% respectively. At 10^{-3} M SDS, the chromium recoveries for 0.1, 0.5, and 1.0% of ethanol concentrations were 49%, 50%, 48%, respectively. This is seen from Figure 4.27 as the tridimensional plot obviously. As it is seen from the figure that at higher concentrations of surfactant and ethanol, the recoveries did not change and low values were observed for all the ethanol concentrations.

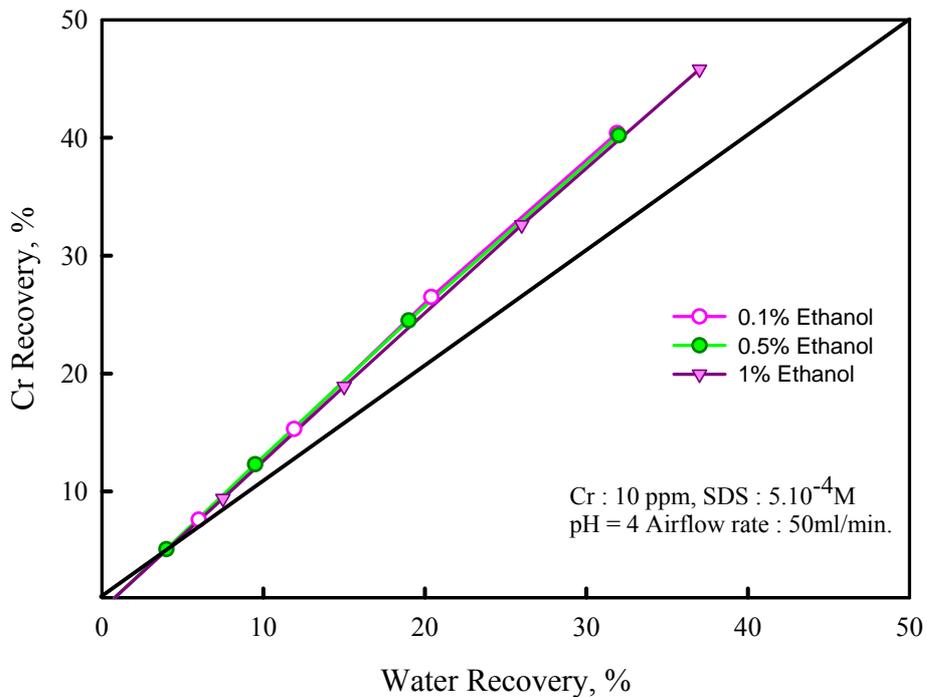


Figure 4.25. Chromium Recovery as a Function of Water Recovery. (Initial Chromium Concentration: 10 mg/L; pH: 4, SDS : $5 \cdot 10^{-4}$ M)

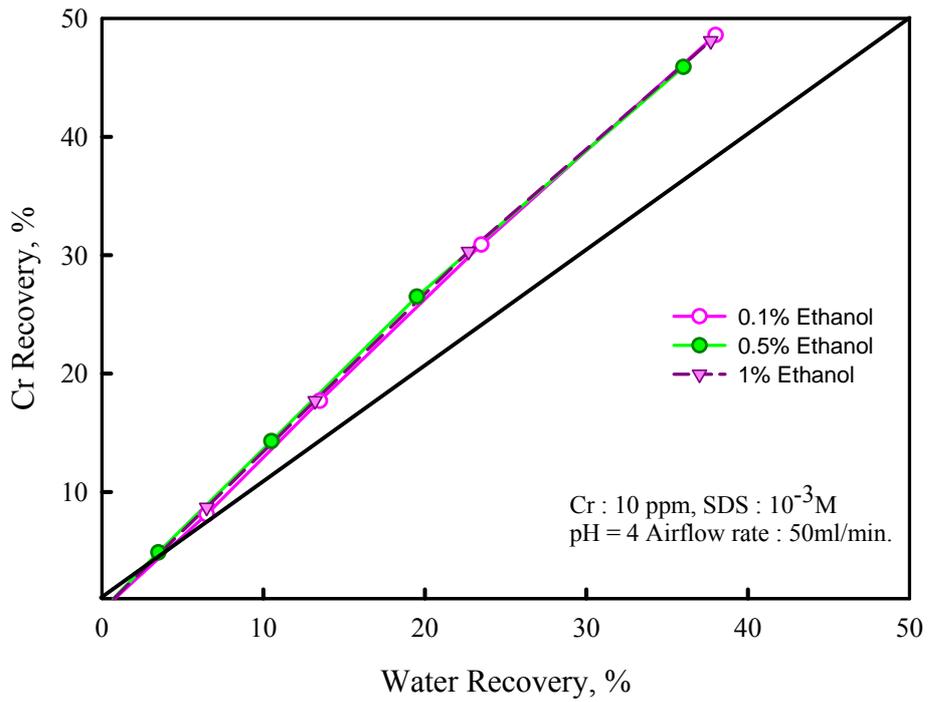


Figure 4.26. Chromium Recovery as a Function of Water Recovery. (Initial Chromium Concentration: 10 mg/L; pH: 4, SDS : 10^{-3} M)

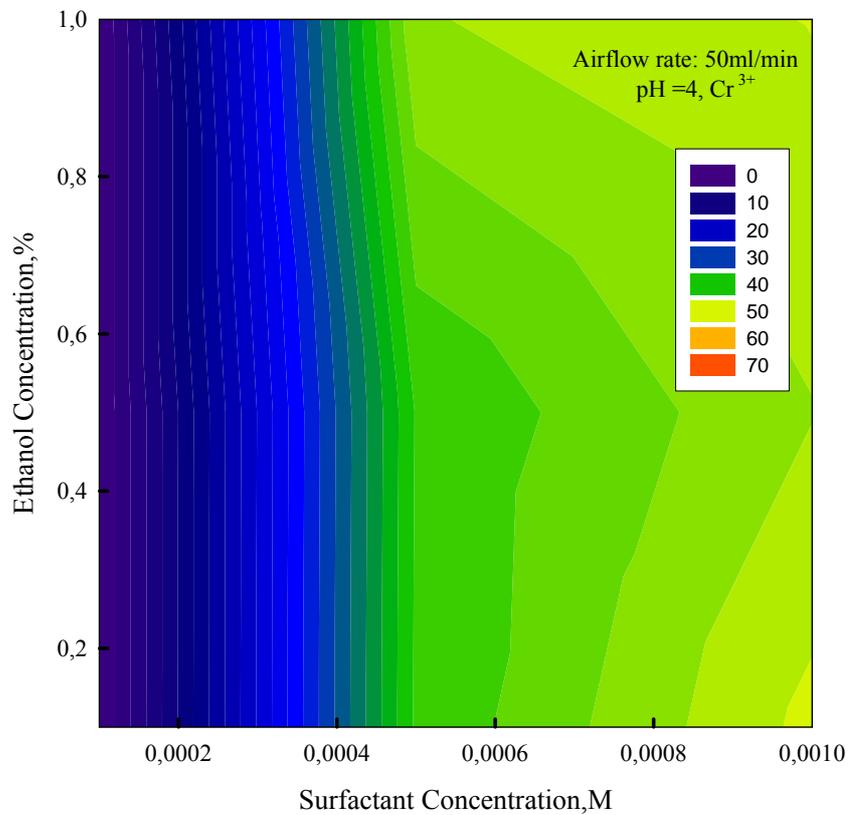


Figure 4.27. Effect of Ethanol and Surfactant Concentrations on Chromium Recovery as a Function of Time. (Initial chromium concentration: 10 mg/L; pH: 4)

4.5. Effect of Water Chemistry

4.5.1. pH of the solution

4.5.1.1. Copper

The effect of solution pH on ion flotation was also tested since there is a distribution of ionic species for varies pH values (see Figure 4.5). The results of these experiments were presented in Figure 4.28 for copper. The sign of the charge of copper ion was positive at pH values of 6, 8 and 10 and therefore anionic surfactant, SDS, was used. The highest recovery was obtained in the presence of 5.10^{-4} M of SDS at pH 10 (90%). The recoveries were 66% and 35% for pH 6 and 8, respectively. On the other hand, since the sign of the species present at pH 12 was negative, a cationic surfactant, HTAB, was used. The results of the experiments were obtained in the presence of 5.10^{-4} M of HTAB at pH values of 10 and 12 were also given at Figure 4.28. The recoveries obtained were 48% and 79% for pH 10 and 12, respectively. It is observed from the figure that anionic surfactant, SDS, had no influence on the copper recovery at pH value of 12 compared to cationic surfactant, HTAB.

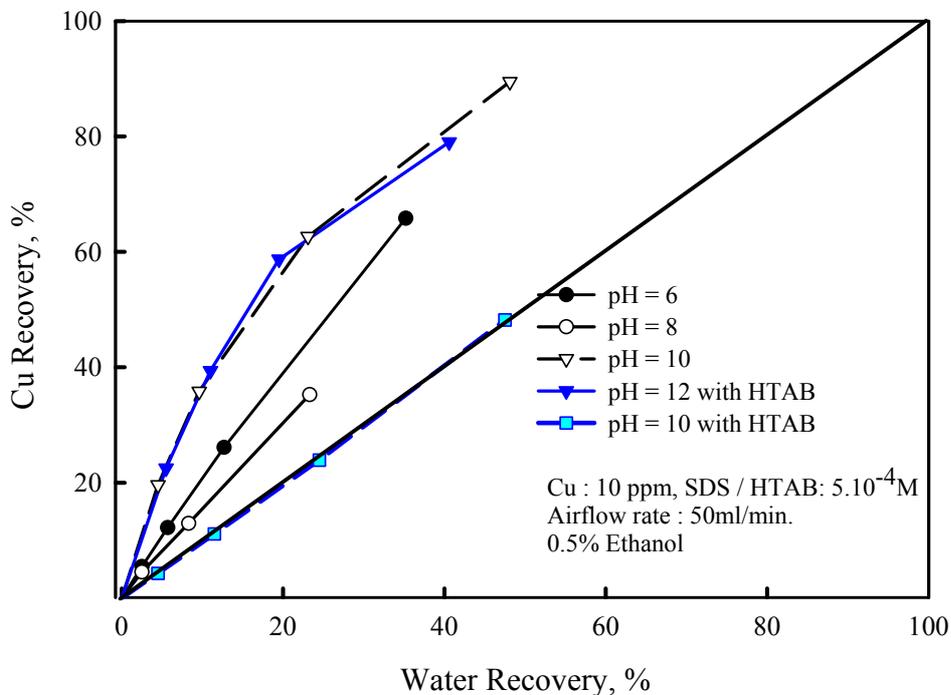


Figure 4.28. Copper Recovery as a Function of pH. (Initial copper concentration: 10 mg/L)

4.5.1.2. Zinc

The effect of solution pH on zinc flotation was tested since there is a distribution of ionic species for varies pH values (see Figure 4.6). Figure 4.29 shows the recovery of zinc as a function of pH. The sign of the charge of zinc ion was positive at pH values of 6, 8 and 10 and therefore anionic surfactant, SDS, was used. There was no flotation at pH 10. However, the recoveries of 68% and 71% were obtained in the case of pH 6 and 8, respectively. The dominant species were negatively charged at pH of 12 and therefore a cationic surfactant, HTAB was used and the recoveries of zinc at pH of 10 and 12 were obtained as 46% and 72%, respectively. As it is seen in Figure 4.29, there was no recovery at pH of 10 in the presence of SDS compared to HTAB because of using low ethanol concentration (0.1%).

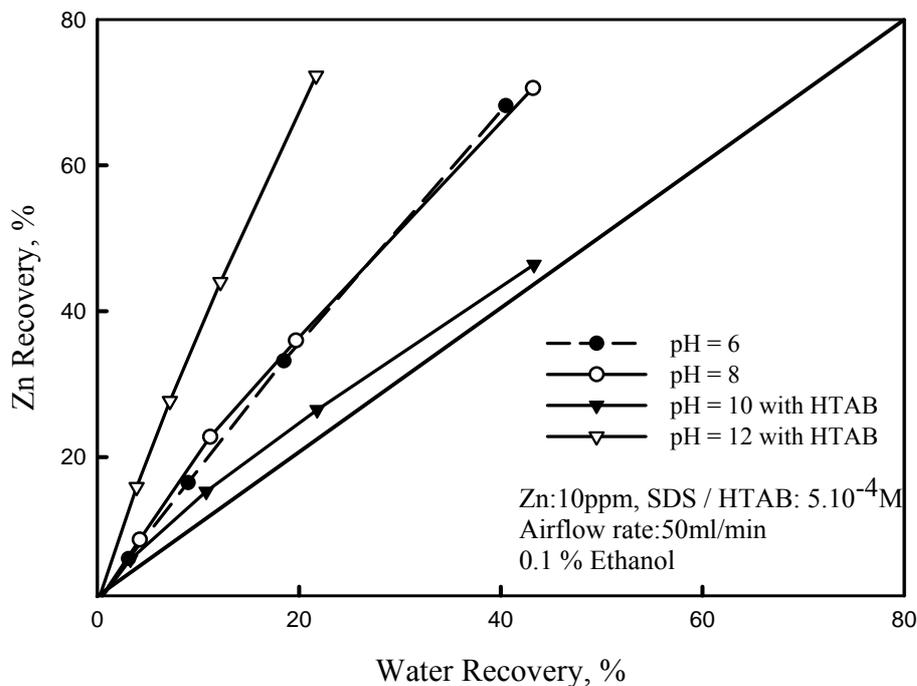


Figure 4.29. Zinc Recovery as a Function of pH. (Initial Zinc Concentration: 10 mg/L)

4.5.1.3. Silver

The effect of pH of solution on silver recovery was tested since there is a distribution of ionic species for varies pH values (see Figure 4.7) and presented in Figure 4.30. As it is seen in Figure 4.7, at pH values of 6, 8, 10 silver is positively charged and therefore anionic surfactant, SDS, was used. The recoveries of 25% 73% and 72% and were obtained in the case of pH 6, 8 and 10 respectively. The best recovery of silver is 10^{-4} M SDS, 0.1% MIBC and pH value of 4. The dominant species were negatively charged at pH of 12 and therefore a cationic surfactant, HTAB were used and the recoveries of silver at pH of 10 and 12 were obtained as 47% and 71%, respectively. Figure 4.30 showed that HTAB was not effective at pH of 10 compared to SDS.

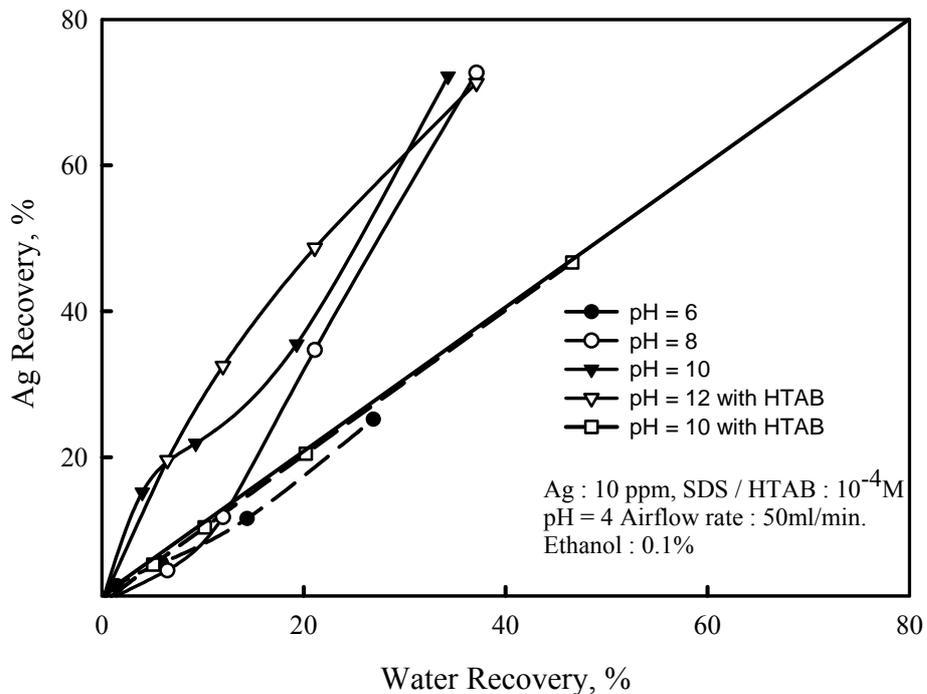


Figure 4.30. Silver Recovery as a Function of pH. (Initial Silver Concentration: 10 mg/L)

4.5.1.4. Chromium

The effect of solution pH on chromium recovery was tested since there is a distribution of ionic species for varies pH values (see Figure 4.8) and presented in Figure 4.31. According to Torem, 2001, the highest chromium removal occurs in the pH range 4 – 6. As it is seen in Figure 4.8, at pH values of 6, 8, 10 chromium is positively charged and therefore anionic surfactant, SDS, was used. The recoveries of 36% , 97% and 29% were obtained in the case of pH 6, 8 and 10 respectively. However, in Figure 4.27, at pH value of 4 the recovery of chromium was around 50% for the same condition (10^{-4} M SDS, 0.1% MIBC). The dominant species were negatively charged at pH of 12 and therefore a cationic surfactant, HTAB were used and the recoveries of chromium at pH of 10 and 12 were obtained as 48% and 86%, respectively.

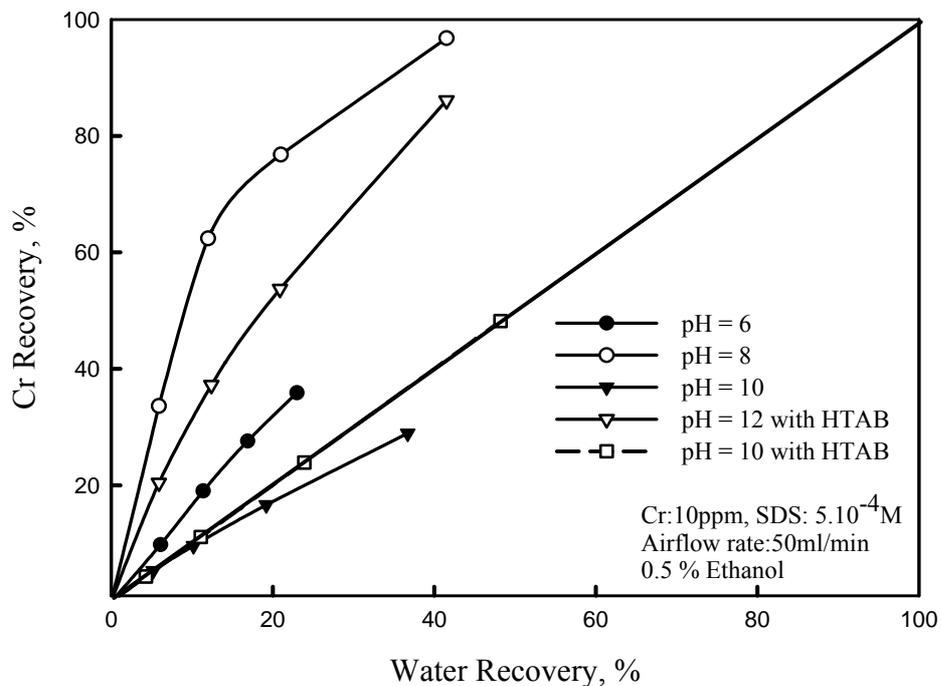


Figure 4.31. Chromium Recovery as a Function of pH. (Initial Chromium Concentration: 10 mg/L)

4.5.2. Ionic Strength

In this part of the study, the effect of ionic strength was studied. For this purpose a tap water with Na^+ , Mg^{2+} , Ca^{2+} ions were used. The average concentrations of those elements are given in Table 4.1:

Table 4.1. Concentrations of Na, Ca, Mg in Tap Water Used in Studies.

Element	Na	Ca	Mg
Concentration (mg/L)	18	200	26

The results of this study were given in Figures 4.32, 4.33, 4.34 and 4.35. These experiments were done at different concentrations as 10, 50 mg/L (for copper, zinc and chromium) and 100 mg/L (for silver).

As it is seen from the Figure 4.32, the copper recoveries decreased from 89.5% to 43% and from 88% to 44% in the case of tap water for 10 and 50 mg/L concentrations respectively. In Figure 4.33, zinc recoveries decreased for 10 and 50 mg/L, from 69% to 39% and from 41% to 42%, respectively. The recovery of chromium gave the similar reduction as seen in Figure 4.35. The recoveries reduced from 97% to 95% for 10 mg/L and from 90% to 82% for 50 mg/L concentrations. In Figure 4.34, results for silver recoveries decreased from 73% to 51% and from 41% to 40% for 10 and 100 mg/L respectively.

This drastic decrease can be explained by the presence of excess Na, Mg, Ca ions that compete with copper. So the metal ions can not find enough dodecyl sulfate molecules to attach to. Analysis of these ions (Ca, Mg and Na) were also conducted in the froth samples to prove this. It was found out that 98% of the ions present in the cell was floated.

In Figure 4.35, chromium concentration was increased to 50 mg/L in the presence of 5.10^{-4} M SDS and 0.5 % ethanol at pH 8, the recovery decreased to 81%. It might be because of the high number of chromium ions compared to the surfactant molecules. The number of chromium ions is equal to 11.6×10^{19} and 58×10^{19} in case of 10 mg/L and 50 mg/L respectively. The number of surfactant molecules, on the other

hand did not changed and stayed as 30.1×10^{19} which is not enough for 50 mg/L chromium concentration.

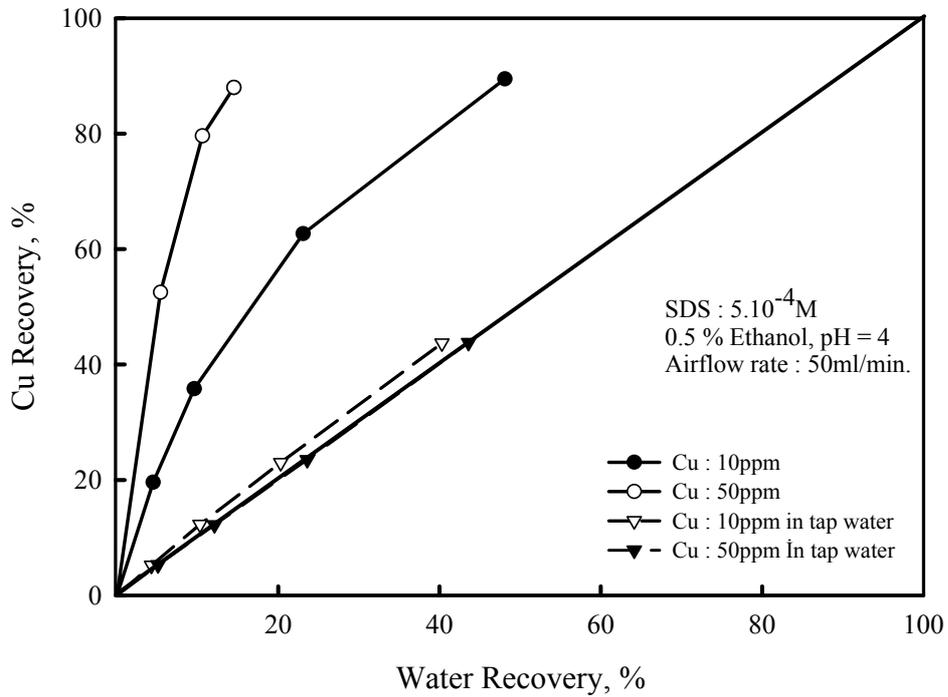


Figure 4.32. Effect of Ionic Strength on Copper Recovery. (SDS: 5.10^{-4} M, 0.5% Ethanol, pH: 4, Airflow rate : 50 mL/min.)

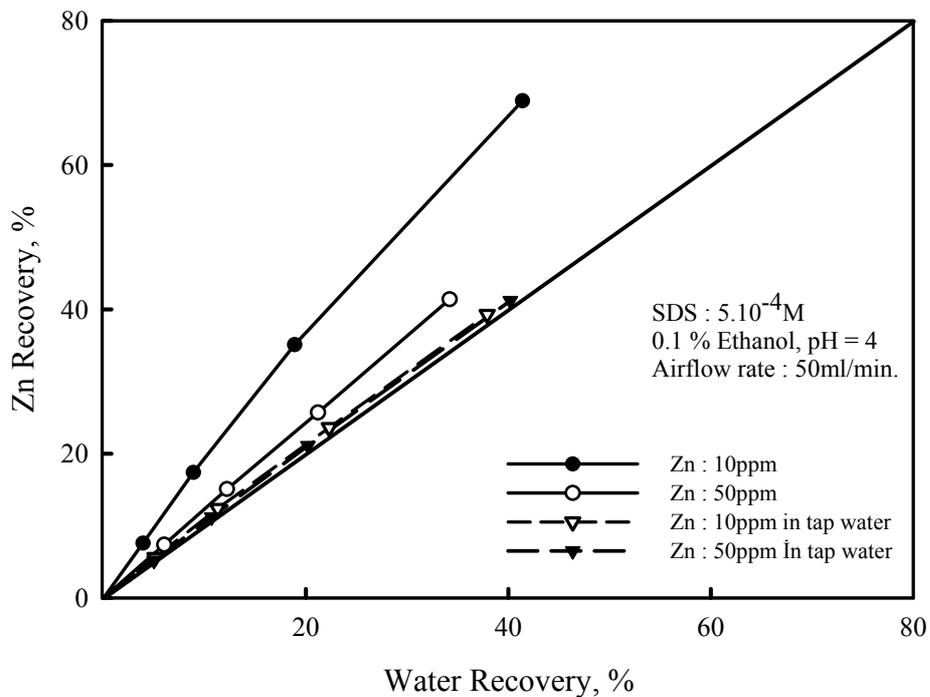


Figure 4.33. Effect of Ionic Strength on Zinc Recovery. (SDS : 5.10^{-4} M, 0.1% Ethanol,

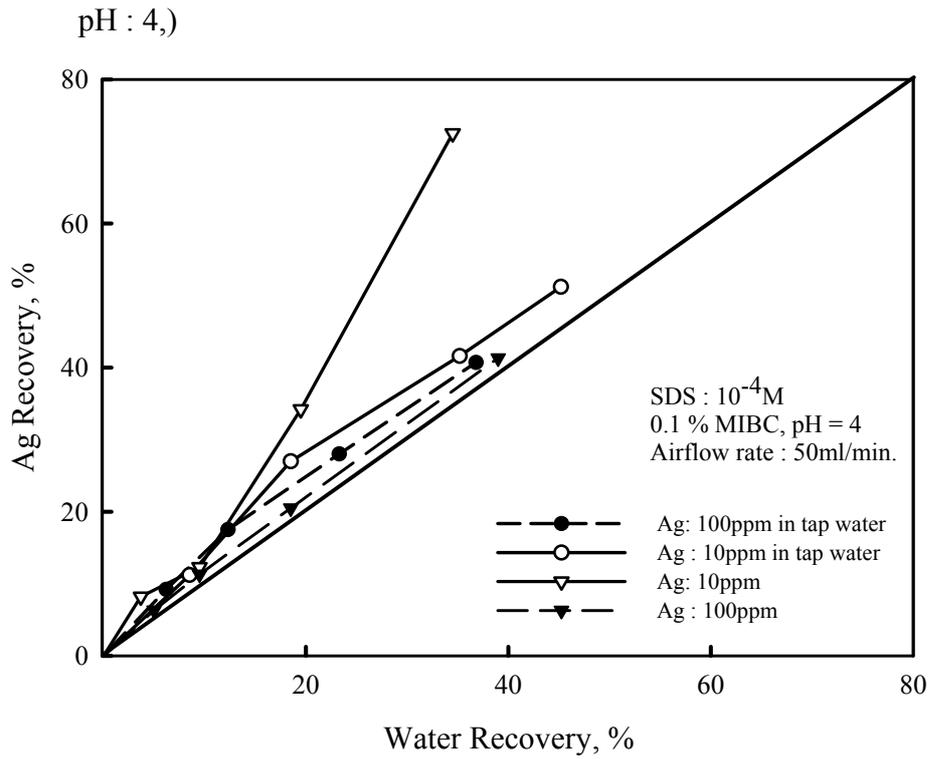


Figure 4.34. Effect of Ionic Strength on Silver Recovery. (SDS : 10^{-4} M, 0.1% MIBC, pH : 4, Airflow rate : 50 mL/min.)

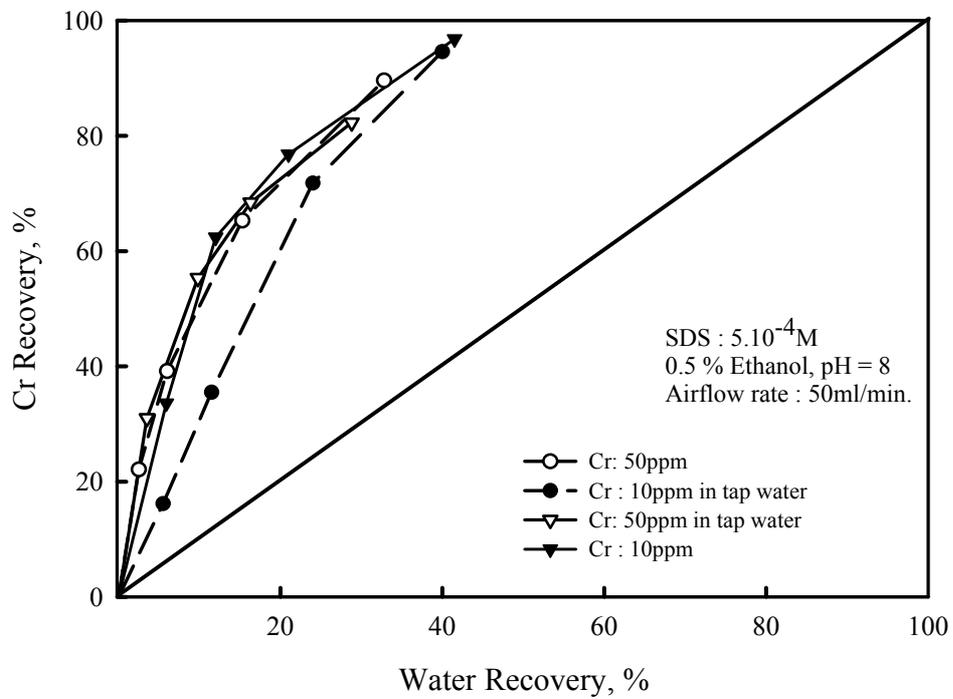


Figure 4.35. Effect of Ionic Strength on Chromium Recovery. (SDS : 5.10^{-4} M, 0.5% Ethanol, pH : 8, Airflow rate : 50 mL/min.)

4.6. Selective Flotation

In this part of the study, metal ions were floated selectively when they are present together. Metal solutions contained copper, zinc, chromium and silver. The results were presented for different compositions of metal solutions in Figures 4.36, 4.37 and 4.38 in the presence of 5.10^{-4} M SDS with varying ethanol amount and pH.

In order to separate the metals from each other, three different flotation experiments were performed. The first flotation experiment was done to separate copper from chromium, zinc and silver solution. The first solution was prepared by using the condition that had given the best recovery of copper (5.10^{-4} M SDS, 0.5% of ethanol and pH value of 10).

As it is seen in Figure 4.36, when silver was present in the solution of copper (10 mg/L), zinc (10 mg/L) and chromium (10 mg/L), small amount of silver precipitated as silver chloride and separated selectively. The rest remained in the cell due to its very low flotability (30%). So copper and chromium were separated from zinc and silver. The recoveries of copper and chromium floated was 77% and 81%. The recovery of zinc was only 45%. This shows one that zinc can not be removed separately.

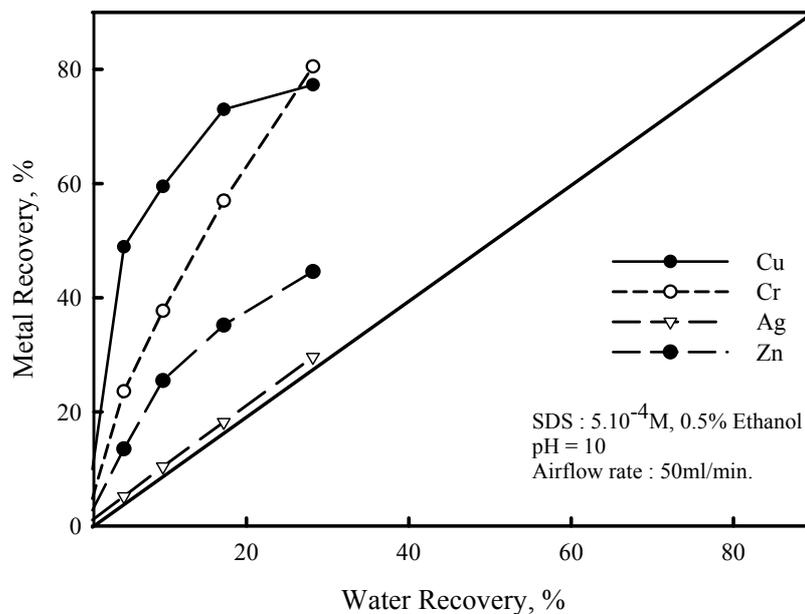


Figure 4.36. Selectivity Results of Copper, Zinc, Silver and Chromium. (SDS: 5.10^{-4} M, 0.5% Ethanol, pH : 10, Initial Metal Concentration (Cu, Cr, Zn, Ag) : 10 mg/L)

The second flotation experiment was connected to separate chromium from copper and zinc solution and the result is given in Figure 4.37. The pH of the solution was equal to 8. The initial metal concentrations were 10 mg/L for each of them. The recoveries obtained were 86%, 60% and 58% for chromium, zinc and copper, respectively. This shows the possibility that chromium separation from the solution that has zinc and copper under this conditions.

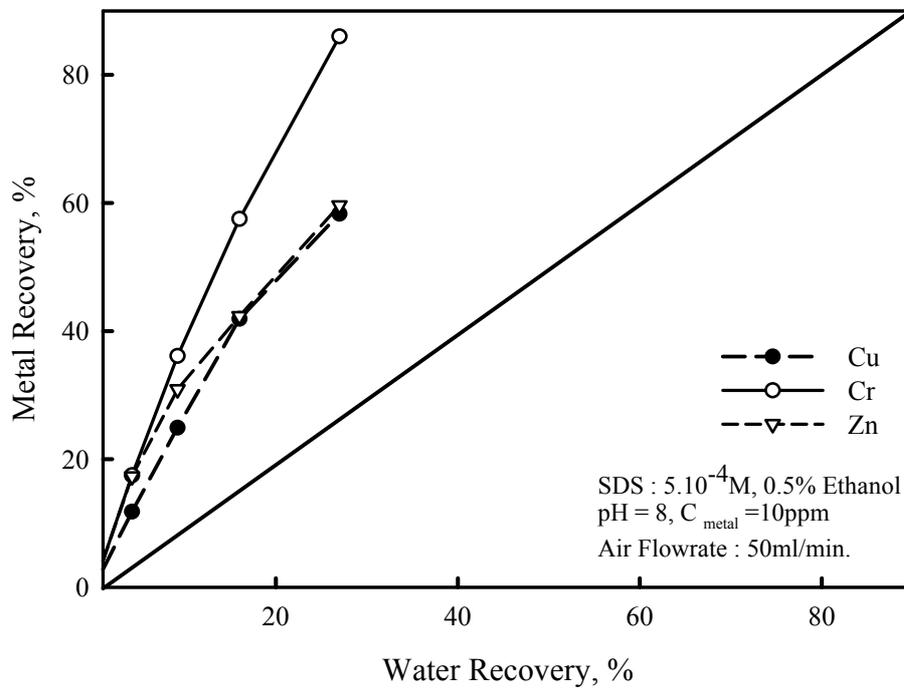


Figure 4.37. Selectivity Results of Copper, Zinc and Chromium. (SDS : 5.10^{-4} M, 0.5% Ethanol, pH : 8, Initial Metal Concentration : 10 mg/L)

The third flotation experiment was performed to separate zinc from the solution mixture of copper and chromium. In this case the conditions were different. Changing the pH and the ethanol concentration as 4 and 0.1%, respectively made the separation possible. The recoveries were 72% for zinc, 31% for chromium and 27% for copper. As seen in Figure 4.38, the selective flotation of Zn is possible under these conditions. Because this is the best condition for zinc not for others.

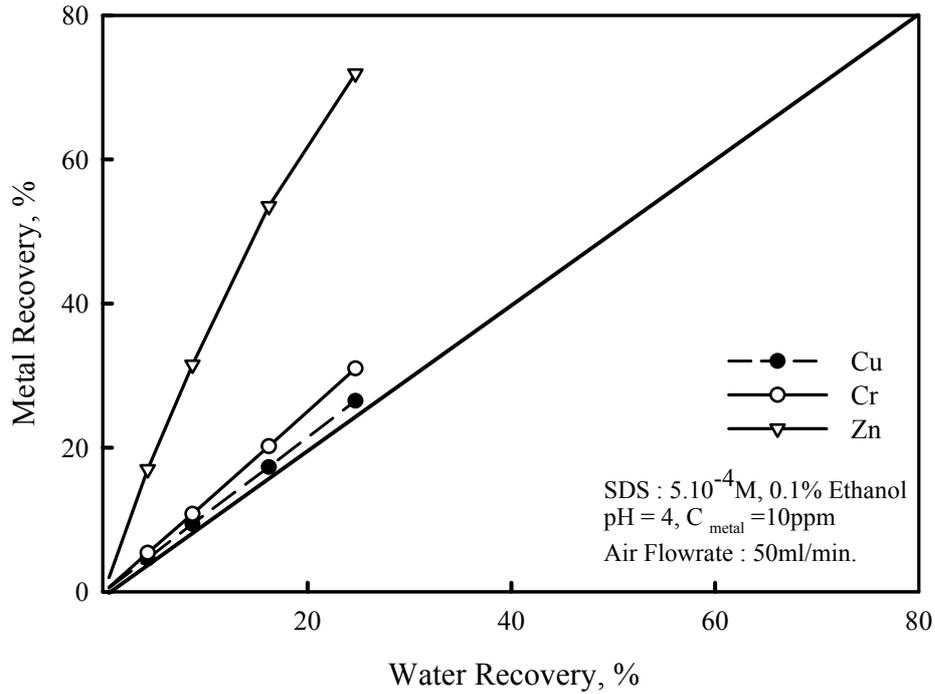


Figure 4.38. Selectivity Results of Copper, Zinc and Chromium. (SDS : 5.10^{-4} M, 0.1% Ethanol, pH : 4, Initial Metal Concentration : 10 mg/L)

4.7. Kinetic Studies of Metals

The curve fitting results of the flotation kinetics equations are given in Figures 4.39 and 4.40 for the case of best recoveries for Cu, Zn and Cr. A number of kinetic equations were fitted the data to determine the best phenomenological model and these equations are given in Table 4.2 (Polat and Chander, 2003). The classical first order model (Panu, et. al, 1976) describes the hydrophobic particles flotation having a constant flotability (Eqn. 4.5). For the case of a monodisperse feed, where all particles have the same flotability, the equation is expressed by:

$$R(t) = R_{\infty} (1 - e^{-kt}) \quad (4.5)$$

where R is the recovery at time t, R^* is the ultimate recovery for an infinite time, and k is the rate constant.

It was observed that the classical first order equation fitted the data as good and better than any of the other equations in Table 4.2. hence the results given in Figures 4.39 and 4.40 are for the Classical First-Order Flotation Kinetics Equation. It can be seen from the Figure 4.39 that Zn floats not only more in amount but also floats faster

than Cu since its flotation rate (0.120 min^{-1}) is almost twice as large as that of Cu (0.059 min^{-1}).

The fact that the Classical First-Order Flotation Kinetics Equation fitted the data better than other equations means that the floatable species of copper and zinc in solution have flotation probability similar to each other for each ion. That is, all the copper ions in solution show similar floatability to other copper ions whereas all the zinc ions are similar to the other zinc ions in solution. Even though this seems not surprising, it is an indirect indication that surfactant-ion pairs are similar and show similar floatability for the case of each ion-surfactant pair.

Another important observation that somehow flotation of zinc and chromium seem to follow the first-order kinetics when compared to copper. This may have several reasons such as a faster and better interaction of the zinc and chromium ions with the surfactant which results in a rapid surfactant-ion pair which then interacts in a first-order fashion with the air bubbles. If the surfactant-ion interactions were slower compared to the flotation rate, then secondary effects would play a role and the flotation process would not follow a first-order rate equation as was the case for copper. However, the data is not sufficient to speculate further on such behaviour.

Standart errors and R^2 values were also determined for copper, zinc and chromium. R^2 values were obtained as 0.9913, 0.9995 and 0.9916 and standart errors were determined as 0.0282, $4.27 \cdot 10^{-3}$ and 0.0205 for copper, zinc and chromium, respectively.

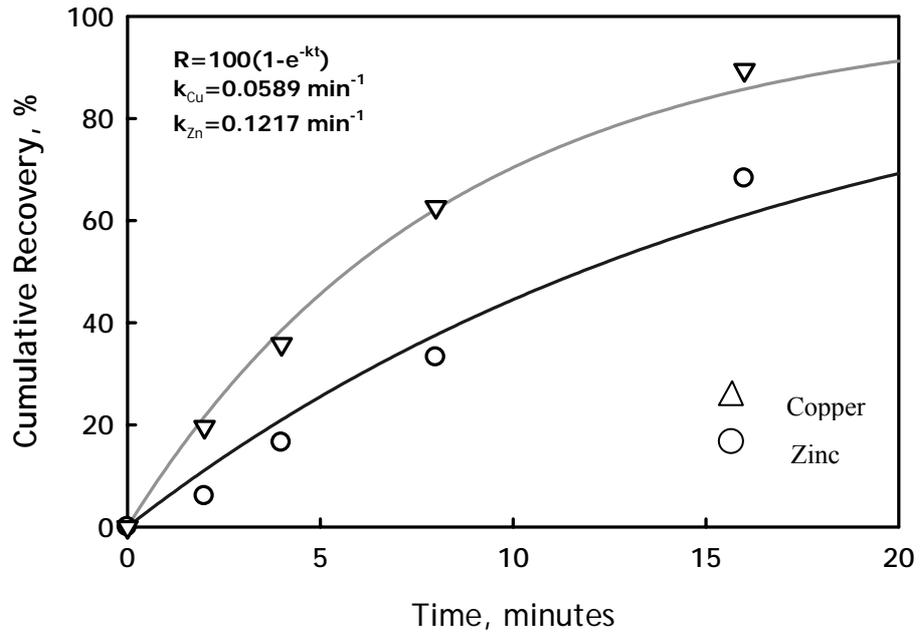


Figure 4.39. The Results of the Flotation Kinetics for Copper and Zinc

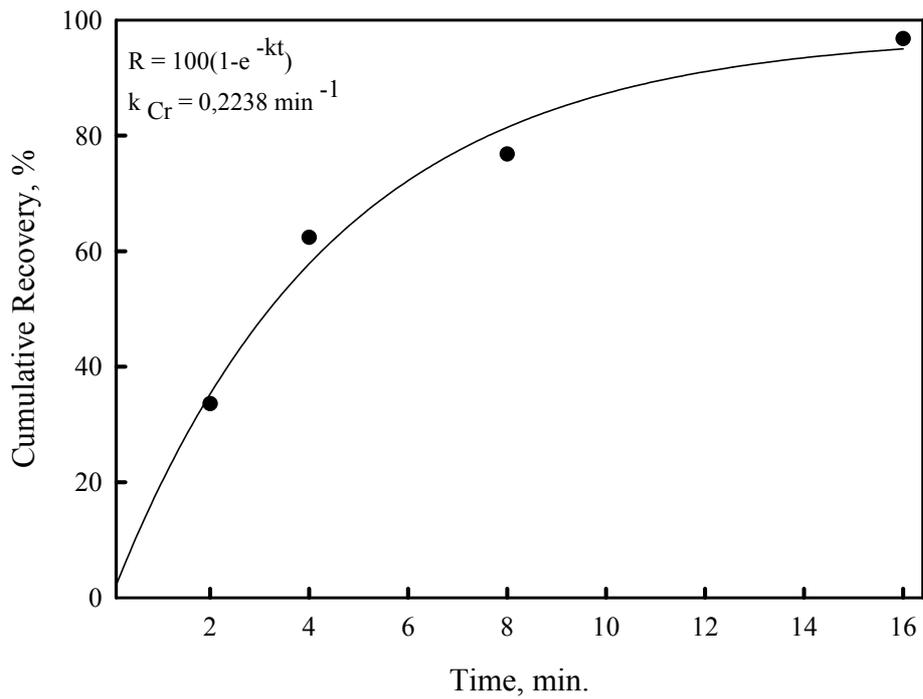


Figure 4.40. The Results of the Flotation Kinetics for Chromium.

Table 4.2. The First-Order Models with Distribution of Flotation Rate Constants Tested for the Cu and Zn Recovery.

Model	$1 - R(t) / 100$
Classical First-Order Equation	e^{-Kt}
First-Order Equation with Rectangular Distribution of Flotation Rates	$\frac{e^{-\mu t + \frac{wt}{2}} - e^{-\mu t - \frac{wt}{2}}}{wt}$
First-Order Equation with Triangular Distribution of Flotation Rates	$\frac{e^{-\frac{wt}{2}} + e^{-\frac{wt}{2}} - 2}{e^{-\mu t} (\frac{wt}{2})^2}$
First-Order Equation with Sinusoidal Distribution of Flotation Rates	$\frac{e^{-\mu t + \frac{2wt}{3}} - \frac{2wt}{\pi} e^{-\mu t - \frac{2wt}{6}}}{1 + (\frac{2wt}{\pi})^2}$
First-Order Equation with Gamma Distribution of Flotation Rates	$\frac{(\mu + \sigma^2 t)^{-\frac{\mu^2}{\sigma^2}}}{\mu}$
First-Order Equation with Normal Distribution of Flotation Rates	$\frac{\text{erf}(\frac{\sigma t + \frac{\mu}{\sigma}}{\sqrt{2}}) - \text{erf}(\frac{\sigma t - \frac{\mu}{\sigma}}{\sqrt{2}})}{2e^{\mu t - \frac{\sigma^2 t^2}{2}}}$

CHAPTER 5

CONCLUSIONS

In this study, ion flotation experiments were performed to investigate the removal of heavy metals (copper, zinc, silver and chromium) from wastewaters. Various parameters such as pH, surfactant and frother concentrations and airflow rate values were tested to determine the optimum flotation conditions. Sodium dodecyl sulfate (SDS) and Hexadecyltrimethyl ammonium bromide (HTAB) were used as collectors depending on the charge of metal species which changes as a function of solution pH. Ethanol / MIBC were used as frothers. Based on the findings of these studies, the following main conclusions can be obtained:

1. For 10 mg/L copper, the recovery was obtained as 73.6% in the case of 0.5% ethanol and $5 \cdot 10^{-4}$ M SDS concentration at pH 4. For 50 mg/L copper, the recovery decreased to 41.8% due to insufficient number of surfactant molecules present. For different pH values, especially pH of 10, the recovery increased to 89.5%. At pH of 12, instead of SDS, HTAB was used as cationic surfactant (because of the negative charge of copper) and the recovery was obtained 79.0%. At pH of 10 HTAB had no effect on copper recovery (48.2%).
2. For 10 mg/L zinc, the highest recovery was obtained as 68.9% in presence of 0.1% ethanol and $5 \cdot 10^{-4}$ M SDS concentration at pH 4. For 50 mg/L zinc, the recovery decreased to 41.4%. It can be explained that the number of surfactant molecules (30.1×10^{19}). For pH values as 6 and 8, the recoveries of 68,2% and 70,6% were obtained respectively. At pH 10 and 12, the cationic surfactant, HTAB was used. In the case of pH 12 the recovery was 72.3%. while it was low in the case of pH 10.
3. For 10 mg/L silver, the varying ethanol concentrations had no influence on the silver flotation for all the pH range. Another type of frother known as methly isobutly carbinol (MIBC) was used and the highest recovery was obtained as 72.5% in the case of 10^{-4} M SDS, 0.1% of

MIBC and pH 4. For 100 mg/L silver, the recovery decreased to 41.3% depending on the high number of silver ions (5.58×10^{20}) compared to the surfactant molecules (30.1×10^{19}). Increasing pH values did not affect the silver recoveries and the best recovery was at pH 4. At pH 12, HTAB was used and the recovery was 71.3%. When HTAB was used at pH 10, the recovery decreased because of the positive charge of silver.

4. The recovery of chromium was low at pH of 4 for several different concentrations of SDS and ethanol. The best recovery was obtained at pH 8 (96.8%). At pH 12, HTAB was used and the recovery was 86.1%. At pH 10, HTAB had no effect on the recovery.
5. Increasing the ionic strength of water decreased the recoveries most probably due to the presence of excess Na, Mg, Ca ions that competed with metals for surfactant molecules.
6. Selective flotation experiments were also conducted in the presence of metal ion mixture solutions. It was possible to separate copper and chromium from zinc and silver under suitable conditions. However, zinc could not be removed separately. It was also possible to separate chromium from zinc and copper and zinc from copper and chromium under suitable conditions.
7. The classical first order equation fitted the results. Zinc and chromium floated not only more in an amount but also floated faster than copper since their flotation rates (0.120 min^{-1} and 0.224 min^{-1}) were almost twice as large as that of copper (0.059 min^{-1}).
8. MIBC was more effective to decrease surface tension at air/water interface compared to ethanol. The surface tension data was used to calculate the area (25.3 \AA^2) that one SDS molecule occupies at air/water interface.

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APPENDIX A

SURFACE TENSION

Table A.1 Surface Tension Values of Sodium Dodecyl Sulfate (SDS).

Surface Tension (dyn/cm)	SDS Concentration	Surface Tension (dyn/cm)	SDS Concentration	Surface Tension (dyn/cm)	SDS Concentration
71,3	0,0002	56,3	0,003	38,46	0,011
70,48	0,0004	55,6	0,0032	38,46	0,012
69,6	0,0006	51,7	0,004	38,46	0,0135
69,3	0,0008	47,12	0,005	38,46	0,014
67,9	0,001	43,8	0,006	38,46	0,0155
66,15	0,00142	41,3	0,007	38,46	0,0168
64,4	0,00175	39,04	0,008	38,46	0,0179
62,5	0,002	38,46	0,01	38,46	0,019
59,8	0,00236	38,46	0,0104	38,46	0,021

APPENDIX B

FORMS OF METALS IN WATER

Forms of Copper (10 – 50 mg/L) in Water

Table B.1. Speciation Table of 10 mg/L Copper in Water as a Function of pH.

pH	Cu(OH)_2	Cu(OH)_3^-	Cu(OH)_4^{2-}	Cu^{2+}	$\text{Cu}_2(\text{OH})_2^{2+}$	$\text{Cu}_2\text{OH}^{3+}$	$\text{Cu}_3(\text{OH})_4^{2+}$	CuOH^+
2	8,7224E-17	1,86E-25	1,65E-36	1,574E-04	5,466E-15	4,1E-12	4,769E-25	4,5E-10
3	8,7249E-15	1,86E-22	1,66E-32	1,574E-04	5,467E-13	4,1E-11	4,771E-21	4,5E-09
4	8,7228E-13	1,86E-19	1,65E-28	1,573E-04	5,464E-11	4,09E-10	4,768E-17	4,5E-08
5	8,6995E-11	1,85E-16	1,65E-24	1,569E-04	5,435E-09	4,07E-09	4,729E-13	4,49E-07
6	8,4226E-09	1,79E-13	1,6E-20	1,519E-04	5,095E-07	3,82E-08	4,292E-09	4,35E-06
7	4,5724E-07	9,74E-11	8,67E-17	8,25E-05	1,502E-05	1,12E-07	6,867E-06	2,36E-05
8	3,6912E-06	7,87E-09	7E-14	6,66E-06	9,785E-06	7,33E-09	3,613E-05	1,9E-05
9	1,796E-05	3,83E-07	3,41E-11	3,24E-07	2,316E-06	1,73E-10	4,16E-05	9,27E-06
10	6,868E-05	1,46E-05	1,3E-08	1,24E-08	3,387E-07	2,54E-12	2,327E-05	3,54E-06
11	4,979E-05	1,061E-04	9,45E-07	8,98E-11	1,78E-09	1,33E-15	8,866E-08	2,57E-07
12	6,5004E-06	1,385E-04	1,23E-05	1,17E-13	3,035E-13	2,27E-20	1,973E-12	3,35E-09
13	3,8968E-07	8,3E-05	7,39E-05	7,03E-17	1,091E-17	8,17E-26	4,251E-18	2,01E-11

Table B.2 Speciation Table of 50 mg/L Copper in Water as a Function of pH.

pH	$\text{Cu}(\text{OH})_2$	$\text{Cu}(\text{OH})_3^-$	$\text{Cu}(\text{OH})_4^{2-}$	Cu^{2+}	$\text{Cu}_2(\text{OH})_2^{2+}$	$\text{Cu}_2\text{OH}^{3+}$	$\text{Cu}_3(\text{OH})_4^{2+}$	CuOH^+
2	4,361E-16	9,292E-25	8,271E-36	7,868E-04	1,366E-13	1,024E-10	5,960E-23	2,251E-09
3	4,362E-14	9,296E-22	8,276E-32	7,868E-04	1,367E-11	1,024E-09	5,964E-19	2,251E-08
4	4,361E-12	9,294E-19	8,274E-28	7,866E-04	1,366E-09	1,023E-08	5,959E-15	2,250E-07
5	4,348E-10	9,265E-16	8,248E-24	7,841E-04	1,357E-07	1,017E-07	5,903E-11	2,243E-06
6	4,094E-08	8,724E-13	7,766E-20	7,383E-04	1,204E-05	9,015E-07	4,928E-07	2,112E-05
7	1,150E-06	2,451E-10	2,182E-16	2,074E-04	9,496E-05	7,113E-07	1,092E-04	5,933E-05
8	6,765E-06	1,442E-08	1,283E-13	1,220E-05	3,287E-05	2,462E-08	2,224E-04	3,490E-05
9	3,223E-05	6,869E-07	6,115E-11	5,814E-07	7,462E-06	5,590E-10	2,406E-04	1,663E-05
10	1,411E-04	3,007E-05	2,677E-08	2,545E-08	1,430E-06	1,071E-11	2,018E-04	7,281E-06
11	2,399E-04	5,113E-04	4,552E-06	4,327E-10	4,134E-08	3,097E-14	9,920E-06	1,238E-06
12	3,250E-05	6,927E-04	6,166E-05	5,862E-13	7,587E-12	5,683E-19	2,467E-10	1,677E-08
13	1,948E-06	4,152E-04	3,697E-04	3,514E-16	2,727E-16	2,042E-24	5,314E-16	1,005E-10

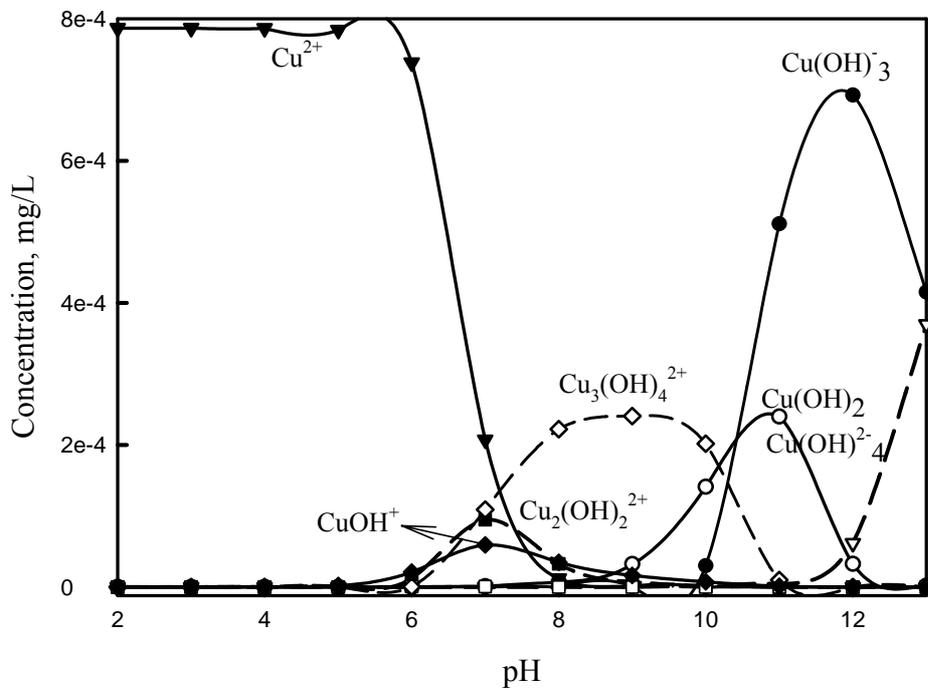


Figure B.1 Forms of Copper (50 mg/L) in Water as a Function of pH

Forms of Zinc (10 – 50 mg/L) in Water

Table B.3 Speciation Table of 10 mg/L Zinc in Water as a Function of pH.

pH	Zn(OH) ₂	Zn(OH) ₃ ⁻	Zn(OH) ₄ ²⁻	Zn ²⁺	ZnOH ⁺
2	2,130E-18	1,114E-26	4,970E-37	1,530E-04	1,384E-11
3	2,131E-16	1,115E-23	4,973E-33	1,530E-04	1,384E-10
4	2,131E-14	1,115E-20	4,973E-29	1,530E-04	1,384E-09
5	2,130E-12	1,115E-17	4,973E-25	1,530E-04	1,384E-08
6	2,129E-10	1,114E-14	4,969E-21	1,528E-04	1,383E-07
7	2,111E-08	1,104E-11	4,928E-17	1,516E-04	1,371E-06
8	1,929E-06	1,009E-08	4,503E-13	1,385E-04	1,253E-05
9	6,322E-05	3,307E-06	1,476E-09	4,539E-05	4,106E-05
10	9,575E-05	5,009E-05	2,235E-07	6,875E-07	6,220E-06
11	2,364E-05	1,237E-04	5,518E-06	1,697E-09	1,536E-07
12	1,996E-06	1,044E-04	4,658E-05	1,433E-12	1,296E-09
13	5,352E-08	2,800E-05	1,249E-04	3,843E-16	3,476E-12

Table B.4. Speciation Table of 50 mg/L Zinc in Water as a Function of pH.

pH	Zn(OH) ₂	Zn(OH) ₃ ⁻	Zn(OH) ₄ ²⁻	Zn ²⁺	ZnOH ⁺
2	1,065E-17	5,570E-26	2,485E-36	7,649E-04	6,918E-11
3	1,065E-15	5,572E-23	2,486E-32	7,649E-04	6,919E-10
4	1,065E-13	5,573E-20	2,486E-28	7,649E-04	6,919E-09
5	1,065E-11	5,572E-17	2,486E-24	7,648E-04	6,919E-08
6	1,064E-09	5,568E-14	2,484E-20	7,642E-04	6,913E-07
7	1,056E-07	5,522E-11	2,464E-16	7,579E-04	6,856E-06
8	9,645E-06	5,046E-08	2,251E-12	6,925E-04	6,265E-05
9	3,161E-04	1,654E-05	7,378E-09	2,270E-04	2,053E-04
10	4,788E-04	2,505E-04	1,118E-06	3,438E-06	3,110E-05
11	1,182E-04	6,183E-04	2,759E-05	8,487E-09	7,678E-07
12	9,978E-06	5,220E-04	2,329E-04	7,165E-12	6,482E-09
13	2,676E-07	1,400E-04	6,246E-04	1,922E-15	1,738E-11

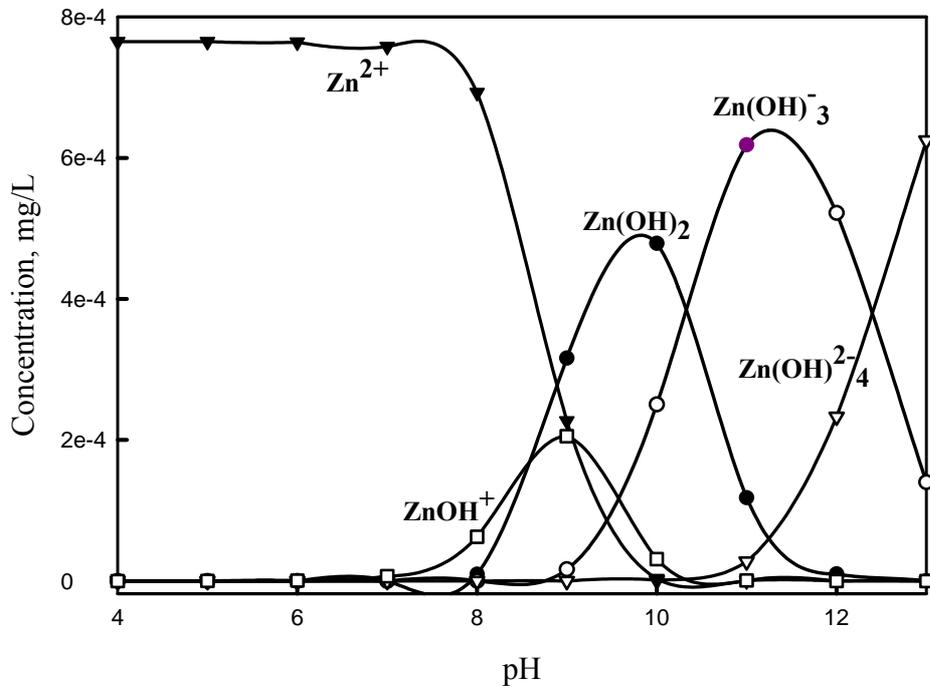


Figure. B.2. Forms of Zinc (50 mg/L) in Water as a Function of pH

Forms of Silver (10 – 100 mg/L) in Water

Table B.5. Speciation Table of 100 mg/L Silver in Water as a Function of pH.

pH	$\text{Ag}(\text{OH})_2^-$	Ag^+	$\text{AgOH}_{(\text{aq})}$	pH	$\text{Ag}(\text{OH})_2^-$	Ag^+	$\text{AgOH}_{(\text{aq})}$
2	9,182E-24	9,271E-04	9,004E-14	8	9,184E-12	9,270E-04	9,004E-08
3	9,185E-22	9,271E-04	9,005E-13	9	9,176E-10	9,262E-04	8,997E-07
4	9,185E-20	9,271E-04	9,005E-12	10	9,096E-08	9,181E-04	8,918E-06
5	9,185E-18	9,271E-04	9,005E-11	11	8,297E-06	8,374E-04	8,135E-05
6	9,185E-16	9,271E-04	9,005E-10	12	3,101E-04	3,130E-04	3,040E-04
7	9,185E-14	9,271E-04	9,005E-09	13	8,366E-04	8,444E-06	8,202E-05

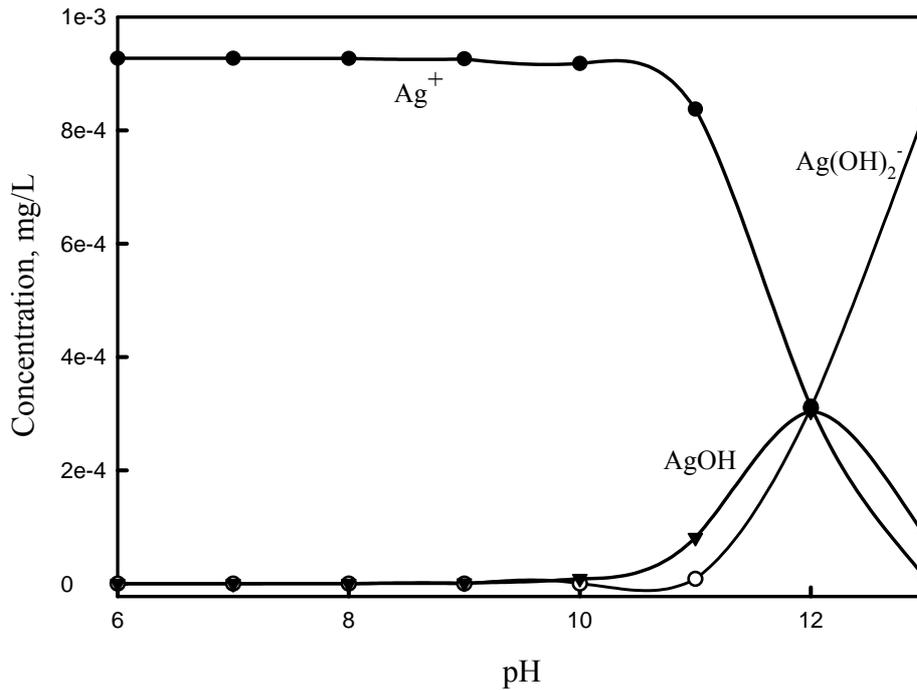


Figure B.3. Forms of Silver (100 mg/L) in Water as a Function of pH

Table B.6. Speciation Table of 10 mg/L Silver in Water as a Function of pH.

pH	Ag(OH) ₂ ⁻	Ag ⁺	AgOH _(aq)	pH	Ag(OH) ₂ ⁻	Ag ⁺	AgOH _(aq)
2	9,18E-25	9,27E-05	9,23E-15	8	9,1847E-13	9,27E-05	9,23E-09
3	9,19E-23	9,27E-05	9,23E-14	9	9,1764E-11	9,26E-05	9,22E-08
4	9,19E-21	9,27E-05	9,23E-13	10	9,0942E-09	9,18E-05	9,14E-07
5	9,19E-19	9,27E-05	9,23E-12	11	8,2795E-07	8,36E-05	8,32E-06
6	9,19E-17	9,27E-05	9,23E-11	12	3,0761E-05	3,1E-05	3,09E-05
7	9,19E-15	9,27E-05	9,23E-10	13	9,1847E-13	9,27E-05	9,23E-09

Forms of Chromium (10 – 50 mg/L) in Water

Table B.7. Speciation Table of 10 mg/L Chromium in Water as a Function of pH.

pH	Cr(OH)_2^+	Cr(OH)_3	Cr(OH)_4^-	Cr^{3+}	$\text{Cr}_2(\text{OH})_2^{4+}$	$\text{Cr}_3(\text{OH})_4^{5+}$	CrO_2^-	CrOH^{2+}
2	1,235E-10	5,320E-15	1,912E-24	1,137E-04	1,203E-09	2,432E-15	2,218E-24	2,560E-06
3	1,029E-08	4,435E-12	1,594E-20	9,475E-05	8,359E-08	1,408E-11	1,849E-20	2,133E-05
4	3,795E-07	1,635E-09	5,878E-17	3,494E-05	1,136E-06	7,059E-09	6,817E-17	7,866E-05
5	4,934E-06	2,126E-07	7,642E-14	4,542E-06	1,921E-06	1,552E-07	8,864E-14	1,023E-04
6	3,226E-05	1,390E-05	4,997E-11	2,970E-07	8,211E-07	4,336E-07	5,795E-11	6,686E-05
7	2,107E-05	9,081E-05	3,264E-09	1,940E-09	3,504E-09	1,209E-09	3,785E-09	4,368E-06
8	2,634E-06	1,135E-04	4,079E-08	2,424E-12	5,473E-13	2,359E-14	4,731E-08	5,459E-08
9	2,671E-07	1,151E-04	4,137E-07	2,459E-15	5,630E-17	2,462E-19	4,798E-07	5,536E-10
10	2,503E-08	1,079E-04	3,877E-06	2,304E-18	4,944E-21	2,026E-24	4,497E-06	5,188E-12
11	1,519E-09	6,545E-05	2,353E-05	1,398E-21	1,820E-25	4,526E-30	2,729E-05	3,148E-14
12	3,079E-11	1,327E-05	4,769E-05	2,834E-25	7,480E-31	3,770E-37	5,531E-05	6,381E-17
13	3,431E-13	1,479E-06	5,315E-05	3,159E-29	9,290E-37	5,218E-45	6,164E-05	7,112E-20

Table B.8. Speciation Table of 50 mg/L Chromium in Water as a Function of pH.

pH	$\text{Cr}(\text{OH})_2^+$	$\text{Cr}(\text{OH})_3$	$\text{Cr}(\text{OH})_4^-$	Cr^{3+}	$\text{Cr}_2(\text{OH})_2^{4+}$	$\text{Cr}_3(\text{OH})_4^{5+}$	CrO_2^-	CrOH^{2+}
2	6,173E-10	2,660E-14	9,558E-24	5,685E-04	3,008E-08	3,039E-13	1,109E-23	1,280E-05
3	5,117E-08	2,205E-11	7,925E-20	4,711E-04	2,066E-06	1,731E-09	9,192E-20	1,061E-04
4	1,765E-06	7,605E-09	2,733E-16	1,625E-04	2,458E-05	7,101E-07	3,170E-16	3,658E-04
5	2,098E-05	9,041E-07	3,250E-13	1,932E-05	3,474E-05	1,193E-05	3,769E-13	4,349E-04
6	1,322E-04	5,696E-05	2,047E-10	1,217E-06	1,379E-05	2,983E-05	2,375E-10	2,740E-04
7	1,053E-04	4,536E-04	1,630E-08	9,690E-09	8,742E-08	1,506E-07	1,891E-08	2,182E-05
8	1,317E-05	5,674E-04	2,040E-07	1,212E-11	1,368E-11	2,949E-12	2,366E-07	2,729E-07
9	1,336E-06	5,755E-04	2,069E-06	1,230E-14	1,407E-15	3,077E-17	2,399E-06	2,768E-09
10	1,252E-07	5,393E-04	1,939E-05	1,152E-17	1,236E-19	2,532E-22	2,248E-05	2,594E-11
11	7,595E-09	3,273E-04	1,176E-04	6,991E-21	4,551E-24	5,658E-28	1,364E-04	1,574E-13
12	1,540E-10	6,634E-05	2,384E-04	1,417E-24	1,870E-29	4,713E-35	2,766E-04	3,191E-16
13	1,716E-12	7,393E-06	2,657E-04	1,579E-28	2,323E-35	6,523E-43	3,082E-04	3,556E-19

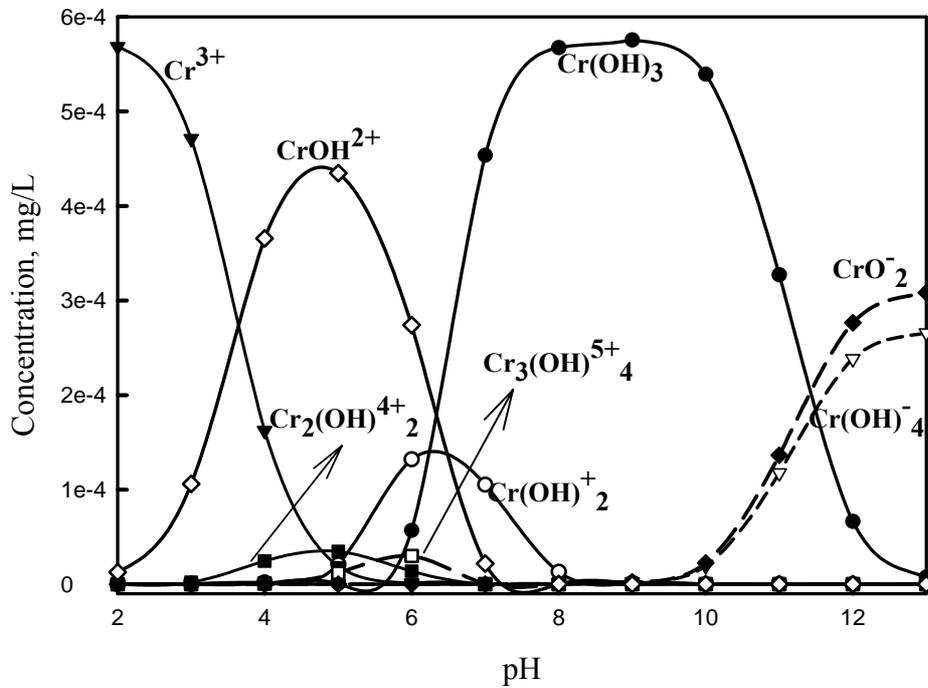


Figure B.4. Forms of Chromium (50 mg/L) in Water as a Function of pH

APPENDIX C

CALCULATION OF FLOTATION RESULTS

Calculation part of the results of the highest recoveries are explained in details in the following tables.

Table C.1. Calculation of the Highest Recovery of Zinc. (Zn : 10mg/L, pH:4, 5.10^{-4} M SDS and 0.1% ethanol)

Time minutes	Weight gram	Weight %	Zn ppm	Zn units	Zn Rec. %	Cum Zn units	Cum. Weight %	Cum. Zn %	Cum. Zn Rec. %
2	39	3,9	16,73	65,25	7,6	65,25	3,9	16,7	7,6
4	50	5,0	16,73	83,65	9,8	148,90	8,9	16,7	17,4
8	100	10,0	15,19	151,90	17,7	300,80	18,9	15,9	35,1
16	225	22,5	12,88	289,80	33,8	590,60	41,4	14,3	68,9
Waste	586	58,6	4,55	266,63	31,1	857,23	100,0	8,6	100,0
Total	1000	100,0		857,23	100,0				

Table C.2. Calculation of the Highest Recovery of Silver. (Ag : 10mg/L, pH:4, 10^{-4} M SDS and 0.1% MIBC)

Time minutes	Weight gram	Weight %	Ag ppm	Ag units	Ag Rec. %	Cum Ag units	Cum. Weight %	Cum. Ag %	Cum. Ag Rec. %
2	37	3,7	37,21	137,68	13,5	137,68	3,7	37,2	13,5
4	58	5,8	33,18	192,44	18,9	330,12	9,5	34,7	32,3
8	100	10,0	26,28	262,80	25,7	592,92	19,5	30,4	58,1
16	150	15,0	9,83	147,45	14,4	740,37	34,5	21,5	72,5
Waste	655	65,5	4,28	280,34	27,5	1020,71	100,0	10,2	100,0
Total	1000	100,0		1020,71	100,0				

Table C.3. Calculation of the Highest Recovery of Chromium. (Cr : 10mg/L, pH:8, 5×10^{-4} M SDS and 0.5% Ethanol)

Time minutes	Weight gram	Weight %	Cr ppm	Cr units	Cr Rec. %	Cum Cr units	Cum. Weight %	Cum. Cr %	Cum. Cr Rec. %
2	59	5,9	43,50	256,65	25,4	256,65	5,9	43,5	25,4
4	61	6,1	31,19	190,26	18,9	446,91	12,0	37,2	44,3
8	90	9,0	22,80	205,20	20,3	652,11	21,0	31,1	64,6
16	205	20,5	15,55	318,78	31,6	970,88	41,5	23,4	96,2
Waste	585	58,5	0,650	38,03	3,8	1008,91	100,0	10,1	100,0
Total	1000	100,0		1008,91	100,0				

Table C.4. Calculation of the Highest Recovery of Copper (Cu : 10mg/L, pH:10, 5.10^{-4} M SDS and 0.5% Ethanol)

Time Minutes (a)	Weight Gram (b)	Weight % (c)	Cu ppm (d)	Cu Units (e)	Cu Rec. % (f)	Cum Cu Units (g)	Cum. Weight % (h)	Cum. Cu % (k)	Cum. Cu Rec. % (l)
2	45	4,5	37,86	170,37	18,6	170,37	4,5	37,9	18,6
4	51	5,1	28,18	143,72	15,7	314,09	9,6	32,7	34,2
8	135	13,5	19,38	261,63	28,5	575,72	23,1	24,9	62,7
16	250	25,0	9,83	245,75	26,8	821,47	48,1	17,1	89,5
Waste	519	51,9	1,85	96,02	10,5	917,48	100,0	9,2	100,0
Total	1000	100,0		917,48	100,0				

To calculate the results of AAS analysis Table C. series were used. In Tables C.1, C.2, C.3 and C.4, first column expresses the time, second column shows the amount of foam, fourth one is the results of AAS analysis. These calculations depend on the mass balance equation. It means the results of addition of weight percents at different time multiply with amount of copper (mg/L), equals to the initial copper concentration (10ppm). Calculations are explained in the following parts:

$$(c) = \text{Weight} * 100 / \text{Total Weight}$$

$$(e) = \text{Weight \%} * (d)$$

$$(f) = \text{Metal Units} * 100 / \text{Total Metal Units}$$

$$(g) = \text{Cumulative Metal Units}$$

$$(h) = \text{Cumulative Weight Units}$$

$$(k) = \text{Cumulative Metal Units} / \text{Cumulative Weight Units}$$

$$(l) = \text{Total Metal Recovery}$$