CHAPTER 1

Introduction

1.1 Introduction

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, chromium, copper, lead, mercury, nickel and zinc are often detected in industrial wastewaters which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture etc. Over the past two to three decades environmental regulations have become quite stringent, warranting effective removal of toxic and hazardous materials and metal ions for the protection of environment, human health and aquatic life.

Many methods are available for the separation of metal ions such as chemical precipitation, adsorption, membrane filtration and electro dialysis. These methods have been developed for heavy metals removal from contaminated wastewaters. Foam separation technique holds promise especially when the metal concentration in aqueous streams is very low.

Chemical precipitation generates sludge which generates extra operational cost for sludge disposal. Adsorbents have low selectivity and production of waste products. Membrane filtration often requires high operational cost due to membrane fouling. Electro dialysis also deals with high operational cost and higher energy consumption. These techniques are not economically attractive when separations from very dilute solutions are involved. Foam separations are particularly attractive for separation problems involving very dilute solutions where most other processes tend to become economically unfeasible.

Foam separation processes are useful for the separation of variety of species ranging from molecular and ionic to microorganisms and mineral fines from one another for the purpose of extraction of valuable products as well as cleaning of wastewaters. Foam separation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment. The attached particles are separated from the suspension by the bubble rise. The targeted substances are separated from bulk water in the foaming phase. The success of this technique depends on the stability and characteristics of foam. The operation is simple with less maintenance as there are no moving parts.

The success of foam separation processes is dependent primarily on the tendency of surface-active species to concentrate at the gas-liquid interface and on their capability to make selected non-surface-active materials hydrophobic by means of adsorption on them or association with them. Heavy metal removal by foam separation has the potential for industrial applications. This can be employed to treat effluent with a metal concentration of even less than 50 mg/l. Although it is only a kind of physical separation process, other advantages such as a better removal of small particles, shorter retention times and low cost make foam separation a promising alternative for the treatment of metal contaminated wastewater.

1.2 Heavy Metals

Heavy metals are elements having atomic weights between 63.5 and 200.6 and specific gravity greater than 5.0. With the rapid development of industries heavy metals in wastewaters are directly or indirectly discharged into the environment, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic.

Heavy metals originating from anthropogenic activities are frequently detected in sediments and water columns of river/lake, which cause a considerable number of the world’s rivers/lakes severely contaminated. Heavy metals pollution had gradually become a major concern worldwide. In aquatic environment, heavy metals are usually distributed as water-soluble species, colloids and in their suspended forms.

However, unlike organic pollutants, natural processes of decomposition do not remove heavy metals. In some conditions, more than 99% of heavy metal entering into river can be stored in river sediments in various forms. However, heavy metals cannot fix in sediment forever. With the variation of the physical–chemical characteristics of water conditions, part of these fixed metals will re-enter the overlying water and become available to living organisms. Heavy metals usually possess significant toxicity to aquatic organisms and then affect human health through food chain. Therefore, investigating the transformation and distributions mechanisms of heavy metal in sediment becomes necessary. (Peng 2009)

Cadmium is present in wastewaters of battery industry , plating baths, mining and acid mine drainage, petroleum refining, paint and pigment manufacturing, motor vehicle and aircraft industries. Table 1.1 lists the cadmium concentrations reported in industrial and municipal waste waters.

Table 1.1: Cadmium concentrations reported for industrial and municipal wastewaters (Poon 1984)

Sources and process	**Cadmium concentration (mg/l)**
Automobile heating control manufacturing	14-22
Plating rinse waters	15 average
Lead mine acid drainage	1000
Municipal raw wastewater	0.008 average

Significant levels of zinc are found in waste waters of steel works with galvanizing lines, zinc plating, acid mine drainage, metal processing, paint manufacturing, textile dying and pigment manufacturing. Heavy metals may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources. Tables 1.2 lists the reported zinc levels in industrial waste waters.

Nickel is found in effluents from battery manufacturing units as well as in the effluents from petroleum industries. Table 1.3 lists the reported nickel levels in industrial wastewaters

Table 1.2: Zinc levels reported in industrial wastewaters (Polat 2007)

Industrial Source	**Zinc concentration (mg/l)**
Metal processing	0.2-1000
Zinc plating	2-1050
Paint manufacturing	0.3-77.4
Textile dyeing	2-6
Pigment manufacturing	0- 1702
Steel works	2.1-1210
Pulp and paper	1.3
Pharmaceutical	0.12
Rubber thread	816

Table 1.3: Nickel levels reported in industrial wastewaters (Hanif 2007)

Industrial Source	**Nickel concentration (mg/l)**
Ghee Industry	34.89
Nickel chrome plating Industry	183.56
Battery Manufacturing Industry	21.19
Tannery Industry	47.26
Textile Industry	31.38

1.3 Effects of Heavy metals on human health

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds.

Cadmium is a trace metal that is very toxic to humans. Cadmium accumulates in the body. Cigarette smokers usually have high levels of cadmium in their body tissues. Cadmium exposure may cause kidney damage. Long-term high cadmium exposure may cause skeletal damage. The itai-itai (ouch-ouch) disease (a combination of osteomalacia and osteoporosis) was first reported from Japan in the 1950's due to cadmium exposure. The exposure was caused by cadmium-contaminated water used for irrigation of local rice fields. Cadmium is toxic at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. Higher exposure can lead to obstructive lung disease.

Zinc is an essential and beneficial element in human metabolism. The daily adult human intake averages 0 to 15 mg /Kg zinc. Excess amount of zinc is harmful to body. Excess amount can cause system dysfuncions that result in impairment of growth and reproduction. The clinical signs of zinc toxicities have been reported as vomiting, diarrhea, bloody urine, liver failure, kidney failure and anemia.

Barakat (2011) has listed the maximum contaminant level standards for cadmium, nickel and zinc as listed in Table 1.4.

Table 1.4: Maximum contaminant level (mg/l)

Heavy Metal	**Maximum contaminant level in wastewater (mg/l)**
Cadmium	0.01
Zinc	0.8
Nickel	0.2

Even though low amounts of nickel are useful in certain body functions such as DNA and RNA stabilization and activation of certain enzymes, excess amounts of nickel are considered carcinogenic.

Table 1.5 lists the most important toxic effects related to metals on human health.

Table 1.5: Most important toxic effects related to metals on humans (Blais 2008)

Metal	**Toxicities**
Antimony	Dermatitis, Keratinis, conjunctivitis and nasal ulceration, possible human carcinogen ,Burning and dryness of the mouth and throat, dysphasia, vomiting, Dermatosis, muscular cramps, facial edema and cardiac abnormalities
Arsenic	Cancers of the lung, skin, bladder, kidneys and liver, damage to respiratory, cardio-vascular, nervous and haematopoietic systems, death
Beryllium	Lung disease, berylliosis, carcinogen, cytotoxicity (impact enzyme function, DNA synthesis, protein phosphorylation, and cell division)
Chromium	Skin irritation, headache, nausea, diarrhea, vomiting, liver and kidney problems, renal failure, irritation of the respiratory tract, emphysema, chronic bronchitis, bronchopneumonia, lung cancer
Copper	Weakness, lethargy and anorexia, abdominal pain, cramps, nausea, diarrhea, vomiting, liver cirrhosis, various diseases, damage to renal tubules, hepatic necrosis, vascular collapse
Lead	Memory and learning deficits, high blood pressure, fertility damage
Mercury	Memory loss, dementia, deficit in attention, ataxia, dysphasia, dizziness, irritability, blindness and deafness
Nickel	Dermatisis, headache, nausea, allergic dermatitis, chronic asthma, coughing, lung fibrosis, cardio-vascular and kidney diseases, lung and nasal cancer
Silver	Irreversible pigmentation of the skin and eyes
Zinc	Depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst, gastrointestinal irritation and vomiting

1.4 Research Objectives:

Foam separation of heavy metals has been studied by numerous investigators particularly in the period of 1960-1980. However, in spite of these studies being reported in the literature on the removal of heavy metals using foaming techniques very limited work exists on the effect of metal ions on the foaming behavior of surfactant Sodium dodecyl sulfate (SDS), sublate characterization and selectivity of metals during separation from binary systems etc. This work is primarily addressed to fill the gaps in our understanding of foam separations. The objectives could be listed as follows:

(i) To evaluate the foaming behaviour of surfactant Sodium dodecyl sulfate (SDS) in the presence of Zn, Cd and Ni and polymer PVP (Poly vinyl pyrrolidone). To image the foam structure using appropriate microscopy.

(ii) To investigate the removal of heavy metals such as Cd, Zn, Ni, Zn-Cd and Ni-Cd from wastewaters by foam separation and establish the optimum conditions in terms of pH, surfactant concentrations, air flow rate etc. in order to remove metals effectively and selectively from waste waters. To evaluate flotation rate constant by performing kinetic studies of metals which can predict cumulative recovery of chosen metal.

(iii) To characterize sublate particles obtained by centrufuging foamate using characterization techniques such as Scanning Electron microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction analysis (XRD), Particle size analysis and Confocal microscopy.

(iv) To investigate the effect of surfactant-polymer association Sodium dodecyl sulfate–Poly(vinylpyrrolidone) (SDS-PVP) on cadmium metal removal and sublate morphology.

(v) To study the effect of scale up and the efficiency of metal removal in larger diameter column.

The thesis is presented in six chapters; ***Chapter 1*: *Introduction*** is devoted to *Introduction* that outlines the nature and scope of the investigation. ***Chapter 2:***

Literature survey provides a review on adsorptive bubble separation techniques with emphasis on foam separation of heavy metals. ***Chapter 3: Materials and Methods*** *describes* Experimental set-ups and materials and methods used in this investigation. ***Chapter 4: Foam formation in aqueous sodium dodecyl sulfate solutions and its characterization*** gives information about liquid holdups of SDS in presence of metals and polymer PVP. ***Chapter 5: Heavy metal removal using foam separation*** describes heavy metals removal and characterization of sublate. Finally, ***Chapter 6: Summary and conclusions*** concludes the investigations carried out in this work.