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Removal of heavy metals from wastewater using electrocoagulation

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<p>Heavy metal contamination of water sources is a constant threat to human health. High exposure of heavy metals have often resulted in severe health hazards such as cancer, growth deficiency, liver and kidney damage and in some extreme cases death (World Health Organization, 2005). Heavy metals are often released into the environment and mainly into the water sources in the form of industrial and municipal wastewater. This thesis aims at examining the possibility of removing 5 different heavy metals from synthetic wastewater using a fairly new technique; electrocoagulation. It also explores the impact of different parameters involved during the electrocoagulation and establishes the optimum levels for the parameters. The parameters whose effects were chosen for study are initial pH of the solution, current density and initial metal concentration. The thesis was approached by doing a literature review of the heavy metals where the impact and characteristics of the chosen metals are first discussed and an overview of current technologies used to remove heavy metals is provided. The experiments were carried out at the environmental engineering laboratory in the Metropolia University of Applied Sciences, Vantaa. The samples were collected at different time intervals between 10 to 40 minutes of the experiment and the residual metal concentration was analysed using the micro plasma atomic emission spectrophotometry (MP-AES). The results showed that the best removal is obtained at a very high pH of 9, current density of 6.25 mA/cm² at the end of 20 minutes for all the metal concentration. The removal rate was found to be significantly dependent on pH of the solution. Higher pH levels resulted in higher removal rate. All the 4 metals showed excellent removal in the majority of the samples apart from manganese. The removal of manganese was found to be most difficult and was only possible at a high pH of 9.</p>	
Keywords	Electrocoagulation, heavy metals, electrodes, current density

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Abbreviations

Cu	Copper
Fe	Iron
Zn	Zinc
Cd	Cadmium
Pb	Lead
Co	Cobalt
As	Arsenic
Hg	Mercury
Se	Selenium
Mn	Manganese
Ni	Nickel
Be	Beryllium
Cr	chromium
Al	Aluminum
Ba	Barium
Sr	Strontium
MCL	Maximum Concentration Limit
WHO	World Health Organization
mA	milli Amps
DC	Direct Current
C.D	Current Density
MP-AES	Micro Plasma-Atomic Emission Spectroscopy

1 Introduction

Classification of heavy metals is still under debate and can be very vague but any elements having relatively higher densities than water and naturally occurring, primarily in earth's crust can be defined as heavy metals. (Lenntech, n.d.) The most common examples include arsenic (As), lead (Pb), zinc (Zn), mercury (Hg), manganese (Mn), copper (Cu), nickel (Ni) and cobalt (Co). While few of the heavy metals are vital to human body in maintaining the metabolism and enzymes, most of the heavy metals found are known to be toxic at different levels to human health, and high exposure to them can be fatal. Several studies have shown the effect of heavy metals to be carcinogenic including organ failures, nervous system breakdown, and long term continuous exposure can lead to death (APEC Water, n.d.).

Exposure to heavy metals can be either via air, water or food. In many areas heavy metal contamination of water streams is also influenced by the human activities, mostly by mining, vehicle emissions, and use of heavy metals containing compounds used in the industries. The wastewaters generated in the industries are released into the environment, mostly into the water streams. Industrial activities, especially electroplating, metal smelting and chemical industries, and manufacturing processes are few sources of anthropogenic heavy metals in water. (Tianrong He, 2007) Poorly treated domestic, industrial, and agricultural wastewater contains high concentrations of metals, which are often discharged into the environment in many developing countries (Gupta, 2008). Zheng found that metals such as mercury and lead after being released into the air through heavy air pollution from vehicles and industries get deposited in the soils around the reservoir which then have the potential to enter the water with the surface runoff (Zheng, 2014). Other natural phenomena contributing to the heavy metal pollution in certain parts of the world include weathering and volcanic eruptions. Hence, heavy metal contamination in the water also depends on the geographical feature, biological and industrial activities of the location.

The level of seriousness of the problem is much worse in developing and poor countries, and they often deploy the maximum concentration limit (MCL) for the metals higher than the proposed WHO limits mainly because of lack of technology, awareness and economic deficiency to treat the metals from their water. As a result, mostly poor people go through the hazards involved in drinking metal contaminated water. (World Bank, 2016)

2 Background

Over the years heavy metals are mostly released into the surface water and environment in the form of untreated/poorly treated wastewater. Consumption of these water sources is the primary exposure route of heavy metals among many countries' population. Apart from that, distribution network pipe's material, condition and length have also been to significantly affect the heavy metal contamination of water in some countries.

Table 1 below lists the sources of heavy metal contamination in drinking water in some of the countries according to the research done by various authors; mentioned in the last column of the table. The table is reprinted from (M.A. Jafar Mazumder, 2016)

Table 1 Sources of heavy metal contamination in drinking water in different countries around the world

Metals	Medium	Location	Sources of contamination	References
Cu, Fe, Zn	Drinking water from the tap in multistory buildings	Dhahran, Saudi Arabia	Corrosion of pipe materials and coatings during water transportation and stagnation in plumbing systems	(I.A.Ilam, 1989)
As, Cd, Hg, Se	Desalinated product water from three plants	Jubail, Al-Khobar, and Al-Khafji, Saudi Arabia	Stabilization and pH adjustment of desalinated water and carryover of metals from source water	(P.C.M. Kutty, 1995)
Pb, Cu, Cd, As, Hg	Drinking water wells and storage tanks	29 cities in the state of Sonora, Mexico	Industrial, mining, and agricultural activities near water sources	(C.J. Wyatt, 1998)
Cd, Cu, Fe, Hg, Mn, Ni	Household drinking water	Riyadh, Saudi Arabia	Corrosion of metal pipes, water tanks, and plumbing systems.	(I. Al-Saleh, 1998)
Cu, Cr,	Surface water	Northern	Soil leaching	(V.

Fe, Mn, Ni	sources for drinking water	Greece		Simeonov, 2003)
Cd, Pb, Zn	Surface water sources for drinking water	Northern Greece	Heavy metal activities and industrial effluents	(V. Simeonov, 2003)
As, Cu, Fe, Pb, Zn	Drinking water	Mount Amiata and downtown Siena, Italy	Leaching from water distribution pipes	(G. Tamasi, 2004)
Cd, Cu, Pb, Zn, Cr	Surface water source for drinking water	Dipsiz stream in Yatagan Basin, Turkey.	Coal-fired power plant	(A. Demirak, 2006)
As, Mn	Groundwater (used as drinking water)	Southern Vietnam and neighboring Cambodia	Geogenic activities, and caused by natural anoxic conditions in the aquifers	(J.B. Buschmann, 2008)
Cd, Cr, Cu, Ni, Pb, Zn	Surface water sources for drinking water	Ranipet industrial area, India	Industrial wastewater effluents and/or dumping of industrial waste	(S.S. Gowd, 2008)
Cd, Cu, Cr, Ni, Pb	Drinking water from WDS and tap	Several islands from nine regions in Greece	Anthropogenic activities, geogenic processes, seawater intrusion	(S. Karavoltzos, 2008)
As, Cd, Pb, Se, Zn	Drinking water from tap	Dakhliya, Egypt	Corrosion of plumbing systems	(M.A. El-Harouny, 2008)
Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Drinking water stored in coolers	Riyadh, Saudi Arabia	Exposure to sunlight, absence of filtration device at the inlet, and aging of coolers	(A.I. Alabdula'aly, 2009)
As	Surface and groundwater sources of drinking water	Patancheru industrial town, Hyderabad, India	Paint, pharmaceutical, fertilizer, and pesticide industries; agricultural activities; As migration from surface to	(A.K. Krishna, 2009)

			groundwater	
Fe, Ni, Pb, Zn	Surface and groundwater sources of drinking water	Patancheru industrial town, Hyderabad, India	Industrial activities	(A.K. Krishna, 2009)
Co, Cr	Surface and groundwater sources of drinking water	Patancheru industrial town, Hyderabad, India	Geogenic processes (natural concentration in granite terrain)	(A.K. Krishna, 2009)
Pb, Cd, Ni, Cu, Cr	Surface water sources from Buriganga River	Dhaka, Bangladesh	Industrial effluents, pesticides, domestic sewage, and tannery industry effluents	(M.K. Ahmad, 2010)
As	Drinking water from shallow tube wells (< 300-m depth)	Floodplain and deltaic and coastal regions of 64 districts in Bangladesh	Subsurface contamination of Holocene floodplain deposits in 59 out of 64 districts	(D. Chakraborti, 2010)
Ni, Cr, Pb, Cu, Hg	Surface water sources in Upper Lake	Bhopal, India	Industrial activities, geogenic processes	(R. Virha, 2011)
Cd, Mn, Pb	Groundwater used as drinking water (tube, deep tube, and ring wells)	Assam, India	Geogenic contamination	(S. Chakrabarty, 2011)
Cd, Pb	Drinking water from WDS and tap	Dakahlia, Egypt	Steel, plastic, and battery industries and household plumbing systems	(R.A. Mandour, 2011)
Cd, Cu, Pb	Groundwater as source of drinking water	Batlagundu, Tamil Nadu, India	Industrial and human activities related to urbanization	(D.S. Thambavani, 2013)
As, Cr, Se	Groundwater wells as	Makkah, Saudi Arabia	Geological features surrounding Makkah	(N.H.M. Khdary,

	sources of drinking water			2014)
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The scale of the problem is well highlighted in the table presented above. Out of many heavy metals, Zn, Ni, Pb, Cu, Cd and As were often detected at high levels in several countries. Countries such as Saudi Arabia, where availability of water is an important issue, supply the drinking water to its people by merging groundwater with desalinated water which brings more metal ions to the drinking water. Analyzing the table further, it can be seen that Cd, Cu, Ni, Pb and Cr contamination in the drinking water is the result of mainly human activities such as industrial activities, urbanization, use of metal laden pesticides and tannery effluents while geogenic factors were traced to be the major sources of arsenic, in addition to some industrial and agricultural activities. Deterioration of supply/ distribution pipes, pipe coatings resulted in high concentration of metals such as Zn, Fe, Cr, Ni and Pb. Meanwhile, Ni in many parts of the world was found in the drinking water as the result of excessive use of chemicals used in water treatment plants.

According to Mosby (C.V. Mosby, 1996), if exposed for a long term 35 metals carry a threat to human health in some form, out of these 23 are heavy metals. It is beyond the scope of this thesis to discuss the impact of every heavy metal in existence. Hence, 5 heavy metals are selected for study in the thesis, whereby the characteristics and impacts of the selected metals are discussed and the removal efficiency of the metals from water using a relatively new technology, electrocoagulation is presented as a result of lab scale experiments.

Electrocoagulation is an emerging prospect which offers an alternative to using chemical coagulants and has been successfully trialed to treat water and waste waters. In addition, in case of arsenic, under right oxidizing conditions, electrocoagulation also offers the possibility of self-oxidation of arsenite to arsenate which then can be removed with ease. Electrocoagulation involves electrolytic oxidation of anode material which results in *in-situ* generation of a coagulant. In recent years, electrocoagulation has generated a great deal of interest in treating water mainly because of its versatility and ease of operation.

Although the initial intention of the thesis was to study the possibility of removing just arsenic, perhaps the most hazardous heavy metal in existence through

electrocoagulation, but due to the lack of equipment and suitable environment to handle the extreme hazards of arsenic compounds needed for the experiments, the idea was reformed to the removal of other heavy metals from contaminated solutions.

3 Heavy metals of interest

As mentioned in the Background chapter, only 5 heavy metals are selected for study in the thesis. The heavy metals were selected because of their availability and the low level of hazards associated with them. For example, even though initially the study of the removal of arsenic (As) was the objective of the thesis, it was not feasible to perform due to of the dangers associated while working with arsenic. Similarly cadmium (Cd) is another heavy metal whose removal from wastewater is as vital as the removal of any other metals chosen for study but because cadmium is so highly carcinogenic and banned from all over Europe, it is not easily available for experiments. The heavy metals of interest are zinc (Zn), nickel (Ni), cobalt (Co), copper (Cu) and manganese (Mn).

3.1 Manganese (Mn)

Manganese is a greyish white, hard, brittle and naturally occurring heavy metal with atomic number of 25. Manganese, as many other heavy metals, is mostly used in alloys such as steel to increase strength and durability. Other uses include additive in gasoline, in paint pigments, in batteries and coloring in ceramics and paints. Manganese also plays an important role in the human body in making bones stronger; it also helps in proper functioning of liver and kidneys. (Duckters education site, c 2017). However, high level of exposure to manganese is extremely dangerous causing neurological disorders, toxicity to the nervous system and is associated to syndromes resembling Parkinsonism especially in children (Department of public health). Infants and young kids are more fragile to manganese poisoning as their bodies are constantly growing and accumulate manganese at a much higher rate than excrete it. Manganese usually get into groundwater streams after being in contact with manganese rich rocks in the aquifer or when naturally present manganese in soil erodes into these water (EPA, 2004). The major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge,

mining and mineral processing, emissions from alloy, steel, and iron production, combustion of fossil fuels, and, to a much lesser extent, emissions from the combustion of fuel additives. (World Health Organization, 2005)

3.2 Nickel (Ni)

Nickel is another heavy metal that is naturally occurring, is lustrous, silvery in color and has an atomic number of 28. Uses of nickel in the industries range from architecture to military, transport, aerospace and marine applications. (Nickel institute, n.d.) Because of its nature of resisting corrosion, is used in alloying with other metals to produce stainless and heat resisting steels. Apart from that, other major uses of nickel is in making batteries including rechargeable ones and is also used with copper together in making coins. (Royal society of chemistry, n.d.). However, long term exposure to nickel has severe health hazards as chronic bronchitis, cancer and reduced lung function have been observed in people who have breathed in nickel laden dusts in the refineries or processing plants (Agency for Toxic Substances and Disease Registry, 2005). Nickel usually gets into the drinking water as a result of air pollution from power plants and waste incinerators which then eventually settle into the soil and gets carried to the groundwater stream as a result of surface runoff. It can also enter in the surface water as a result of discharging poorly treated nickel containing wastewater (Lenntech, n.d.).

3.3 Copper (Cu)

Otherwise, known as *cuprum* in Latin, copper is a reddish orange, soft and ductile metal with atomic number 29. Copper is used in many industries and in daily life. Because of its good electrical conductivity, copper is mainly used in electrical appliances and wirings, like nickel it is also used in alloying of other metals and is used in coins in combination with nickels. Not only in industries but copper can also help in protecting lakes, ponds and rivers as copper sulphate are used to get rid of fungi and algae from the streams. (Royal society of chemistry, n.d.) However, like any other heavy metal, long term exposure to copper can be hazardous causing vomiting, nausea, cramps and in some extreme cases it has been associated with liver and kidney damage. Infants and young children have been associated being more vulnerable to hazards of copper. (Minnesota Department of Health, n.d.). Copper gets into the drinking water as a result of copper pipes used in the distribution network or

household plumbing. When the water sits idle in the corroded copper pipes, it tends to leach the copper and contaminate the tap water. Naturally copper is present in very low amounts in either surface or groundwater. However, as a result of mining, excessive use of agricultural pesticides, manufacturing operations, smelting, industrial discharge and untreated or poorly/treated wastewater released into the water bodies leads to the high concentration of copper in water. (Centers for Disease Control and Prevention, 2015)

3.4 Zinc (Zn)

Zinc is one of the few heavy metals that is actually necessary to be consumed for proper functioning of human body. The heavy metal itself is hard and bluish-white in colour and is found at number 30 in the periodic table. Deficiency of zinc in fetus leads to babies having mental and physical problems after being born. Zinc plays an important role in the manufacture of chemicals in the human cells, which allows in proper functioning of more than 300 enzymes in the human body (DNEWS, 2013). As with little zinc, too much of zinc can be equally hazardous too. Exposure to a huge concentration of zinc has been associated with stomach cramps, skin irritations, vomiting, and nausea, and in some extreme cases, zinc has been proven to have carcinogenic effects, too. In the industrial world, two of the zinc's major uses are galvanizing and making alloys. More than half of the zinc produced worldwide is galvanized with other metals in order to protect it from rusting and corrosion (Chemistry Explained, n.d.). It is also used together with copper in making brass alloy. Zinc mining industries are booming as the demand is always on the rise. Other industrial applications are for example batteries, paints and sun blocks. (Royal society of chemistry, n.d.) Because of its huge use in industrial applications, the wastes and wastewater coming out of these industries carry zinc in large amounts and if not treated satisfactorily, the rivers deposit zinc polluted sludge in their banks. Also zinc is present in fine dust particles in the air as a result of the industrial activities and eventually gets settled in the soil where it stays as solid particles and might seep into the groundwater or water bodies. Hence, removal of zinc from industrial wastewater is very vital. (Charif Gakwisiri, 2012)

3.5 Cobalt (Co)

Like zinc, cobalt is bluish-white in color and has the atomic number of 27 in the periodic table. It has its advantages in human body, when consumed in adequate amounts. Cobalt is used in the body to help absorb and process vitamins B12, it helps in the formation of hemoglobin and regulates and simulates the production of some useful enzymes. Cobalt is used in oil industries and refineries in wide scale, in electroplating, production of glass, paint and enamels, it is also used in making alloys by combining with other metals such as aluminum and nickel. (Royal society of chemistry, n.d.)

Wastewater from nuclear power plants, mining industries, electroplating and many electronic industries contain high concentrations of cobalt, which when released into the water streams, eventually enters the human food chain resulting in high risk of cobalt poisoning. Cobalt poisoning might cause extreme health problems such as low blood pressure, lung diseases, bone defects, diarrhea and paralysis. (Agency for Toxic Substances and Disease Registry, 2004)

4 Heavy metal removal technologies

The dangers of having heavy metals in the food chain and entering our body are well highlighted in the above sections of the thesis. Therefore, it becomes extremely essential in treating and removing as much heavy metals as possible from the wastewater before releasing it to the environment. Due to the development of stricter laws and legislation in wastewater treatment and disposal over the last decades, heavy metals have become priority environmental pollutants and the treatment technologies for removing heavy metals from wastewater is much of an interest and of high importance. There are many methods and technologies in removing heavy metals but the three most used applications in practice are described below.

4.1 Chemical precipitation

Chemical precipitation is the most used removal technology in waste water treatment plants due to its ease of operation (Fenglian Fu, 2010) . Various factors affect the precipitation factor of the metal such as solubility (K_{sp}) of the metals involved, pH of the wastewater, concentration of the metals in the produced wastewater and various

other substances present on it. The process is performed in a way that a used chemical reacts with ions of heavy metals present in the wastewater to form insoluble precipitates of the heavy metals involved such as hydroxide, carbonate, sulphide and phosphate depending on the chemicals used for the precipitation. The formed precipitates are then removed as sludge after coagulation, flocculation, sedimentation and filtration. Removal rate of the metal ions can be optimized with the change in parameters such as pH, temperature, conductivity and metal concentrations. Even though the process is fairly simple, effective and can be inexpensive compared to other removal technologies, further treatment of and disposal of the large amount of concentrated and toxic sludge produced is the major drawback of the process.

4.2 Ion Exchange

Ion exchange is fairly a simple method in removing heavy metals. As the name suggests the method involves exchange of ions present in either synthetic or naturally occurring ion exchanger with that of the metals present in the waste water. Most common natural ion exchangers in use are zeolites. Synthetic ion exchangers are more preferred because of their effectiveness and ability to uptake the majority of the targeted metal ions from the solution (Fenglian Fu, 2010) . When metal contaminated solution is passed through Ion exchangers which are insoluble solid substances the positive charged, possibly toxic metal cations affecting the purity of the water such as of zinc, nickel and copper ions are exchanged with the positive charged ions from the resins such as hydrogen and sodium ions in equivalent amount in the solution, the same goes for negatively charged unwanted anions present in the wastewater solution such as hydroxyl and chloride ions is replaced by sulfate, nitrate and chromate ions released from the resins. The resins can be categorized as either cation or anion exchanger based on the charges of the ions exchanged. (IWA publishing, 2011). The method is highly sensitive to parameters such as pH, temperature, metal concentrations and contact time. (Fenglian Fu, 2010). Although ion exchange processes have advantages ranging from high treatment and removal efficiency to cost effectiveness (low cost and operating materials) but is only applicable in treating low concentrations heavy metals. (IWA publishing, 2011).

4.3 Adsorption

Adsorption is another removal technology in treating heavy metal contaminated wastewater. Adsorption occurs when the solute present in the liquid form in the contaminated wastewater accumulates in the absorbents of either solid or liquid forming a molecular film. (Lakherwal, 2014). Absorbents such as activated carbon, carbon nanotubes, metal oxides and many agricultural and bio absorbents have been tested and proven to be successful in removing metals from waste water. Activated carbon is still the most popular absorbent in use as the removal rate is more than 99% in certain metal ions (IWA publishing, 2011). However, numbers of researchers are still working on to improve the cost of using activated carbon in removing heavy metals. Since the commercial carbon sources are lessening, the prices of using carbon absorbents are increasing every day and also because the activated carbon materials are non-reusable; it becomes essential to find the alternatives without compromising the end result. Bio adsorption is gaining popularity because of its low cost and natural treatment of metal-contaminated wastewater. Cheap and easily available bio adsorbents/ biomass living or dead have been proven to remove heavy metals from wastewater and sludge. Biomass can usually be derived from three sources: 1) non-living biomass, 2) algal biomass and 3) microbial biomass. The most popular among the three and the one that at the moment is of high interest is algal biomass because of algae a renewable natural biomass's wide availability, high treatment efficiency, low cost and high metal sorption capacity. (Fenglian Fu, 2010).

5 Objective

The Objective of the thesis was to study:

- The feasibility of electrocoagulation in removing heavy metals from water
- To assess the impact and optimize the different parameter levels associated with electrocoagulation in removal of heavy metals.

6 Electrocoagulation

Electrocoagulation is an electrochemical method of treating water and wastewater, where sacrificial anodes corrode due to oxidation and dissolve the metal ions from the

anode. Meanwhile, simultaneous formation of hydroxyl ions and hydrogen gas at the cathode results in the formation of precipitates which then later form the floc with the contaminants from the water and can be removed through filtration leaving behind potable water. Electrodes used in the electrocoagulation can be of many metals such as iron, aluminum and platinum. However, till date iron and aluminum have gained the popularity over other metals because of the high removal efficiency, high ion dissolution rates, low in price and the ability to reuse the same metals for several experiments.

Some of the major advantages of electrocoagulation is its ease of operation, pH buffering ability, low sludge production and lower toxic content and easy handling with better settleability. Flocs formed as a result of electrocoagulation are larger, acid resistant, and more stable and hence easy and fast to eliminate through filtration. Since no chemicals are used throughout the electrocoagulation experiments, the treated water is much healthier as opposed to chemical coagulation treatment.

Although very few, there lies some disadvantages in the process such as corrosion of electrodes with time and need to be regularly replaced, formation of an oxide layer on the cathode with time resulting in a decrease in the efficiency of the removal rate and expensiveness of energy consumption for electrocoagulation in some places.

6.1 Theory

An electrocoagulation reactor for heavy metal treatment consists of two sacrificial Fe electrodes; anode and cathode submerged in an electrolytic cell containing metal contaminated water. Which when connected to an external DC power source, the anode metal undergoes electrolytic oxidation releasing ferrous ions (Fe^{2+}), since ferrous ions are soluble they are vital to be oxidized to ferric ions (Fe^{3+}), which can be done by increasing the amount of dissolved oxygen in the solution by sparging air onto the solution containing beaker. However, in many cases air sparging is not necessary as the atmospheric oxidation conditions might suffice the oxidation of Fe^{2+} ions to Fe^{3+} ions which are further hydrolyzed to polymeric hydroxides. Meanwhile, on the cathode side water gets electrolyzed producing hydrogen gas and hydroxide ions. Oxidized Fe^{3+} ions from the anode combines with hydroxides formed on the cathode to form an iron oxide precipitate also known as hydrous ferrous oxide (HFO) which is an excellent coagulant agent. The formed iron oxide then destabilizes the contaminants in the

solution which then aggregates to form floc. The bubble in the solution carries the floc then to the surface through natural buoyancy. The floc can then be removed through filtration after the settling.

Figure 1 below shows the laboratory schematic setup of an electrocoagulation experiment.

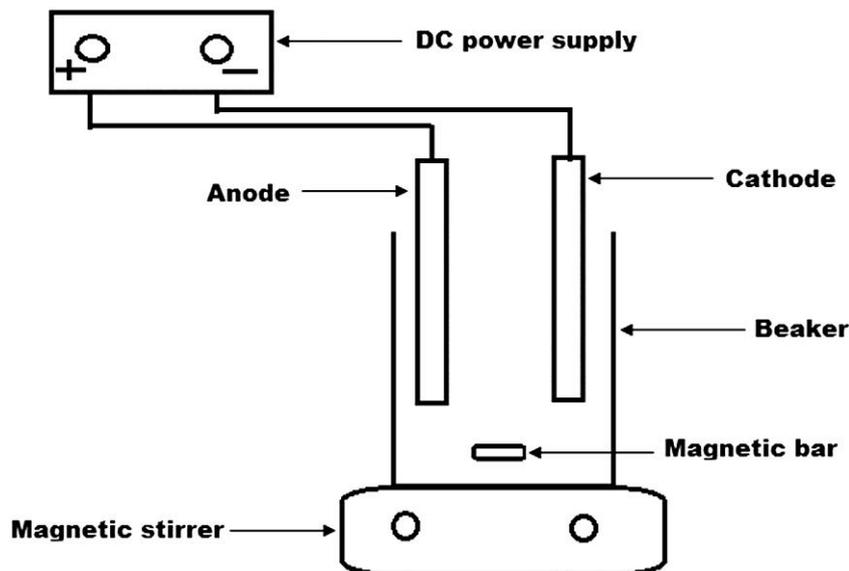
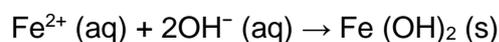
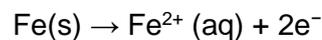


Figure 1 Schematic setup of electrocoagulation system (Verma, 2013)

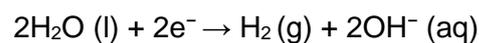
There has been two different mechanism reactions proposed in the electrocoagulation process for iron electrode and they are shown below:

Mechanism I

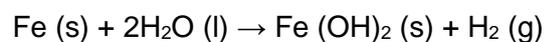
Anode:



Cathode:



Overall:



Mechanism II

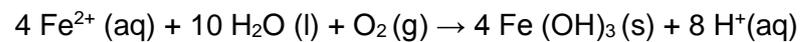
Anode:



Cathode:



Overall:



The mechanism taking place inside the electrolytic cell/beaker is presented below in the Figure below.

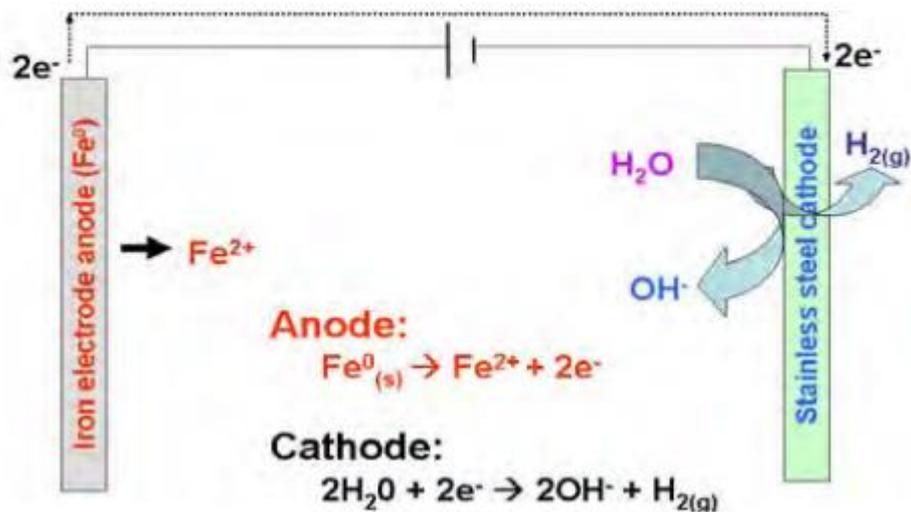


Figure 2 Basic electrolysis reactions inside the electrolytic cell (Divagakar, 2011)

The mass of metal as a result of the oxidation of anode released into the solution, the mass of Fe²⁺, is dependent on the amount of current passed to the solution and can be determined theoretically by Faraday's law given below:

$$m = \frac{I \cdot t \cdot M}{Z \cdot F},$$

where, m is the mass in grams of the ions formed, I is the current applied in Amperes, t is the total amount of electrolysis time in seconds, M is the molar mass of the substance in grams per mole (55.85 g/mol for Fe), Z is the number of electrons transferred per atom (2 for Fe^{2+}) and F is the faraday's constant (96,485 col)

However, (Kuokkanen, 2013) reported that the theoretical amount of anodic dissolution, i.e. the theoretical mass of anions released derived from the above equation is exceeded in real electrocoagulation applications. This phenomenon is referred to as super faradaic efficiency, and the experimental values of anode metal dissolution have varied between 105% and 190% of the theoretically expected value. (Kuokkanen, 2013)

6.2 Materials and methods

6.2.1 Experimental setup

Experiments were performed at the Environmental engineering laboratory in Metropolia University of Applied Sciences, Vantaa. All chemicals used were of reagent grade; hence no further purification was required and were supplied by Sigma Aldrich. Since the metal compounds used in the experiment are hazardous, a material safety data sheet (MSDS) was made for the chemicals used and all the necessary lab precautions were taken.

All the glassware was cleaned thoroughly first with tap water and 1N H_2SO_4 and then again rinsed with distilled water. For the preparation of synthetic metal contaminated wastewater, following chemicals were used:

- For zinc (Zn), zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)
- For nickel (Ni), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- For cobalt (Co), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- For copper (Cu), copper (II) chloride (CuCl_2)
- For manganese (Mn), Manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$)

Stock solutions of concentration 1000 mg/l was prepared separately for each of the five heavy metals by dissolving an appropriate quantity of compounds in distilled water. The synthetic wastewater containing all the five metal ions was then freshly prepared by diluting appropriate volume of each stock solution with distilled water up to 1l. pH of the solution in different experiments was controlled using a diluted NaOH or H₂SO₄ solution as per the requirement.

The electrocoagulation setup in this experiment consisted of a 1l beaker with two iron electrodes separated 0.5cm apart of size 10 cm*4 cm working as anode and cathode were immersed in 1l of metal contaminated synthetic wastewater. The total submerged surface area of each electrode was 40cm². Before each experiment, electrodes were properly scraped with sand paper to remove any scale and then cleaned with successive rinses of 1N H₂SO₄ and water. Using the electrodes without cleaning them prior to every experiment has been proven to decrease the removal efficiency due to passivation/rusting of electrodes with time which results in less iron generation during electrocoagulation (Divagakar, 2011). Constant direct current was applied to the iron electrodes using an external DC power source of approximately 12 V, electric current passing to the electrodes was recorded using a multimeter. In order to ensure the homogenous solution the reactor was placed under the magnetic stirrer and stirred at a rate of 200 rpm throughout the experiments ensuring the proper agitation of the solution. The experiment was repeated at different levels of parameters to find out the optimum level for removal efficiency.

Figure 3 below shows the experimental setup of electrocoagulation experiment performed for this thesis in the laboratory.



Figure 3 Experimental setup of electrocoagulation in the thesis

6.2.2 Parameter levels for experiments

There are several parameters that might be influencing the heavy metal removal efficiency during electrocoagulation. It is beyond the scope of this thesis to study the effect of every possible parameter involved in the electrocoagulation. The thesis discusses the influence and the optimization level of 1) pH of the solution, 2) current density, 3) initial metal concentration and 4) electrolysis time,

It is difficult to map the wastewater pH as there are several parameters that might be influencing the pH in the wastewater such as the different types of metals in the solution, other contaminants and nutrients present in the wastewater. Nevertheless, the pH level of 5, 7 and 9 is selected for the experiments representing an acidic, neutral and basic solution respectively.

Current density is the most important parameter in electrocoagulation as it is the scale of the current density that allows the dissolution of the anode material and generation of Fe ions in the solution. Current density is obtained by dividing the current passed to the electrodes per active surface area of electrodes. Effect of current density on the rate of removal was observed and presented by increasing the current density by two folds after every experiment where current density was chosen for experiments. The

current density for the lab scale experiment was chosen to be 6.25, 12.5 and 25 mA/cm².

Experiments were conducted, and the results were presented as per the observations at the end of 40 minutes. However, the samples were taken out from the beaker during the regular interval of 10, 20, 30 and finally at 40 minutes for the analysis of residual metals and iron in the solution in order to observe the development of the removal process with time. Also the effect of initial metal concentration was investigated by using the solution of metal concentration from 50-150 mg/l and the results were presented showing how increasing the metal concentration affects the removal rate. Effects of other known parameters such as magnetic stirring speed, temperature and distance between the electrodes were not chosen for the study and hence these parameters were kept constant during all the experiments magnetic stirring speed at 200 rpm, room temperature of 22 degree Celsius and distance at 0.5 cm respectively.

6.2.3 Analysis Method

After the electrocoagulation was started i.e. when the current was initially switched on, the samples were collected at 10 minutes interval for every experiment using a polyethylene syringe with a volume of 20 ml, and every sample was double filtered first using 3µm filter pores to remove larger flocs followed by the filtration using 0.45µm filter pores to remove minute flocs. The collected, filtered samples were then analysed for residual Zn, Cu, Co, Ni, Mn and Fe using atomic spectroscopy.

Spectroscopy uses the intensity of light emitted from a flame to determine the quantity in the solution. The machine used for the analysis was 4100 Micro plasma Atomic emission spectroscopy (MP-AES) provided by Agilent technologies which is shown in the figure below.

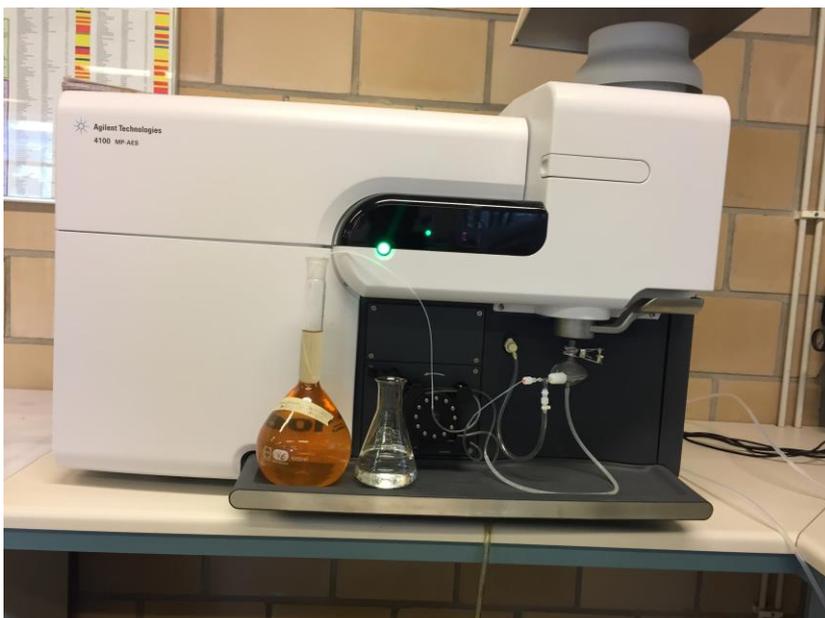


Figure 4 4100 MP-AES Spectroscopy

AES used in the analysis of the solution runs on air using a nitrogen generator. The nitrogen generator supplies an endless supply of nitrogen. Using the nitrogen, plasma is formed in a conventional torch; the formed plasma is a high temperature excitation source which is ideal for sample atomization and excitation producing high intensity emission lines. When the sample aerosol gets inside the torch in the plasma, it is dried, decomposed and then atomized. As the atoms return to lower energy state, they emit light at characteristics wavelengths for each element. These wavelengths of the light then enter the optical system. The fast scanning monochromator then transmits the selected wavelength range onto the solid state CCD detector where spectra and background are measured simultaneously for best precision. (Agilent, 2016)

Figure 5 below depicts the plasma emission on a spectrophotometer.

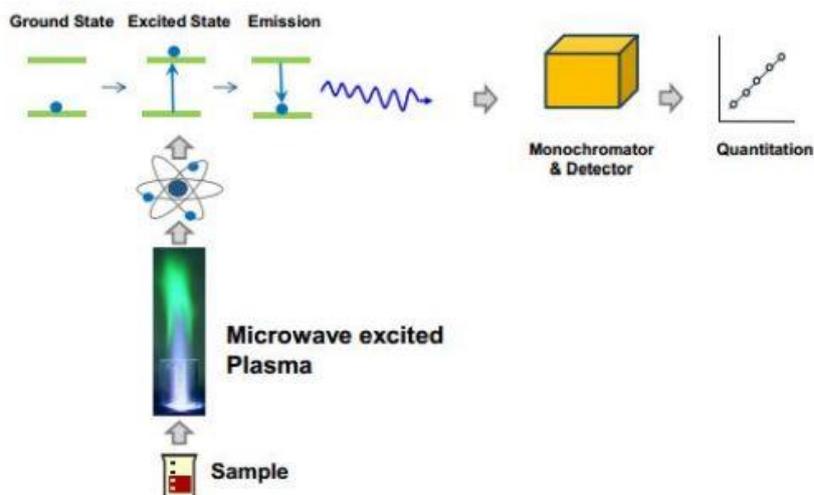


Figure 5 Microwave plasma spectrophotometer light emission (shradar, 2011)

Three standard solutions containing all five heavy metals of interest were prepared of concentrations 2, 5 and 10 mg/l using the same stock solutions made earlier and the calibration curves of metals obtained at known concentrations is then later used to find the concentrations of the heavy metals from the filtered electrocoagulated sample solution. Since the Fe ions are released constantly from the anode throughout the electrocoagulation period, it becomes essential to analyse also the iron concentrations on the final treated water. The standard solutions of the iron concentration of the same levels, 2, 5 and 10 mg/l were also prepared.

After the result of the final concentrations of the metals in the sample, the removal efficiency was then calculated using the following equation:

$$Efficiency \% = \frac{C_i - C_f}{C_i} * 100,$$

where, C_i is the initial metal concentration, and C_f is the final metal concentration after electrocoagulation in mg/l.

6.3 Calibration Curves

Calibration curve can be defined as the standard curve of the solutions at the known concentrations which later is used in order to determine the concentrations of the

substance(s) of the unknown sample. The obtained calibration curves of heavy metals used for the analysis of the concentration of the electrocoagulated sample are shown in figures 6-11 below. The obtained calibration curve also displays the wavelength selected by MP-AES in nanometers (nm) at which the light is emitted for each element.

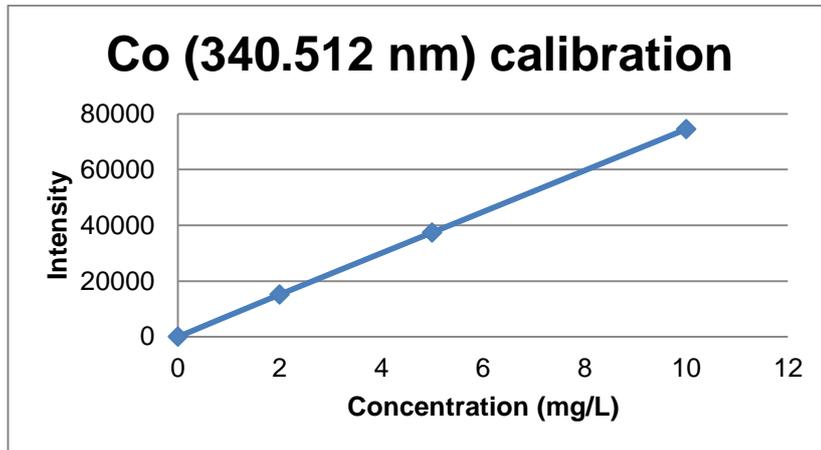


Figure 6 Calibration curve of Cobalt

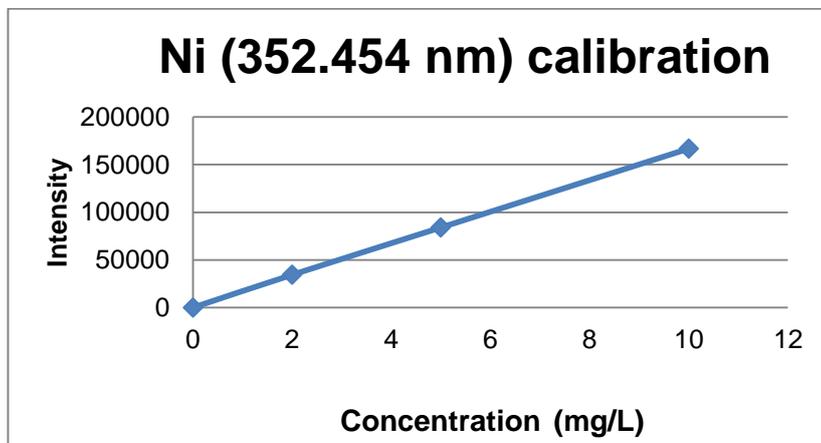


Figure 7 Calibration curve of Nickel

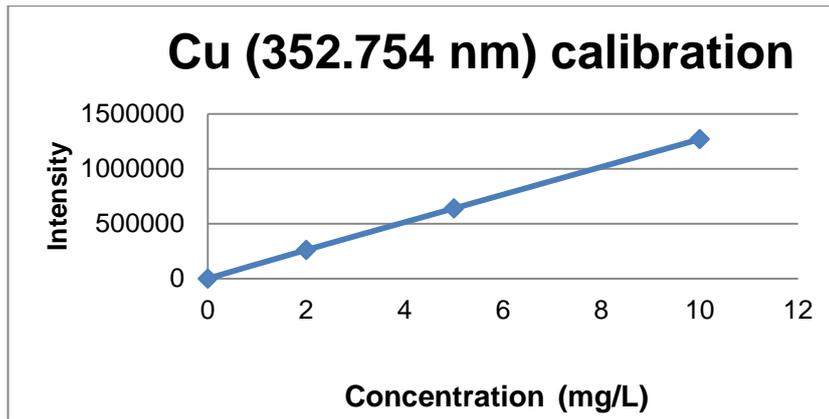


Figure 8 Calibration curve of Copper

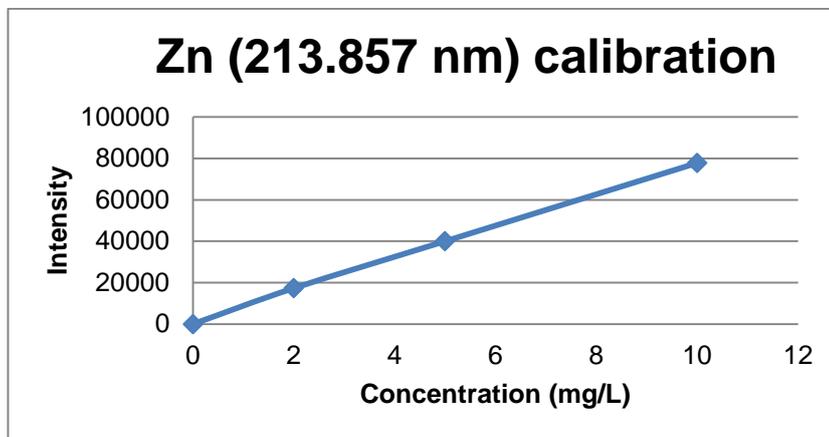


Figure 9 Calibration curve of Zinc

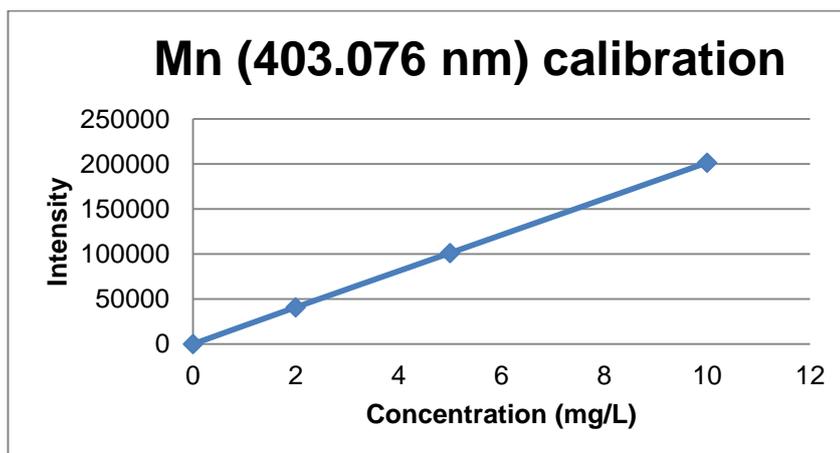


Figure 10 Calibration curve of Manganese

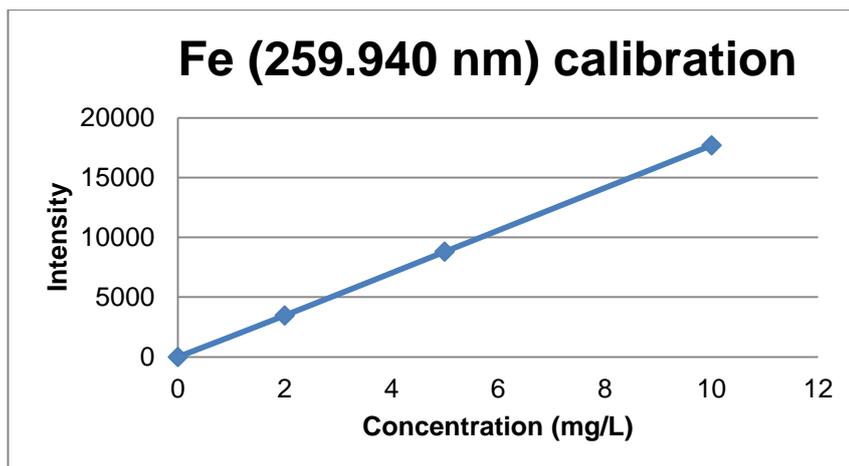


Figure 11 Calibration curve of Iron

7 Results

7.1 Effect of initial pH on removal efficiency

The initial pH had a considerable influence on the removal efficiency of all five metals. During the initial phase of electrocoagulation, slight increase in pH was observed in all the experiments due to the rapid production of iron hydroxide from the electrodes. However, the final pH at the end of 40 minutes was observed to be same as the initial pH for all the experiments.

Effect of pH on removal was tested at a constant current density of 12.5 mA/cm² and constant initial metal concentration of 50mg/L. The removal rate with electrocoagulation increased with the increase in pH which was in agreement with the findings of (Divagakar, 2011). The graph below describes the findings of removal rate at different pH used in the experiments

At pH 9 the removal was at its highest with more than 99% of removal efficiency observed for all the 5 metals at the end of 10 minutes treatment as seen in figure 13. Meanwhile the removal rate was observed to be at its poorest at pH 5 where copper and zinc were the only metals removed at a satisfactory rate of more than 95% at the end of 40 minutes treatment which can be seen in Figure 11. Figure 12 highlights the removal efficiency at pH 7 which was observed to be better than that at pH 5 where zinc and copper were removed at a rate of more than 90% at the end of 10 minutes

treatment, and the final removal efficiency at pH 7 at the end of 40 minutes treatment, was close to 100% for all the metals apart from manganese.

All 4 heavy metals got removed to some extent at all tested pH levels, apart from manganese which was observed to be non-reactive to electrocoagulation treatment unless at high pH of 9.

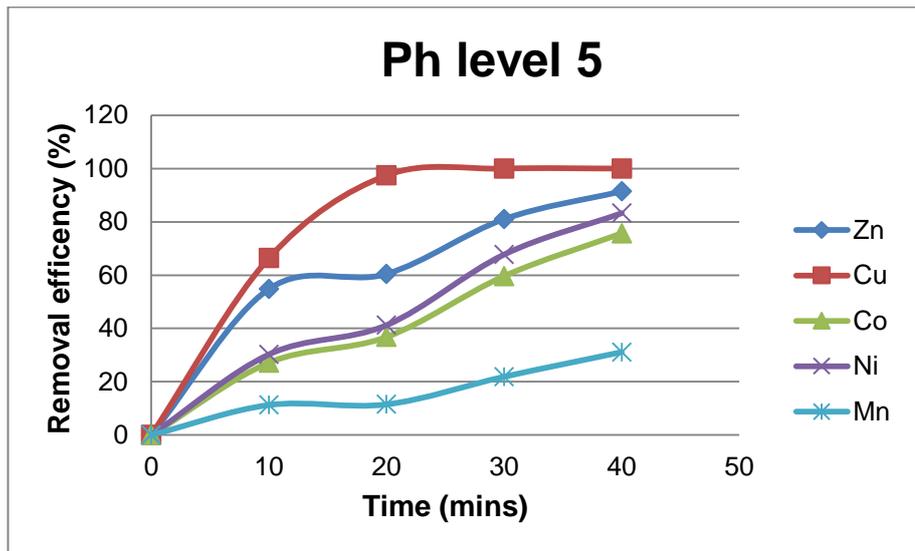


Figure 12 Metals removal at pH 5 at a current density 12.5mA/cm² and at an initial metal concentration of 50 mg/L

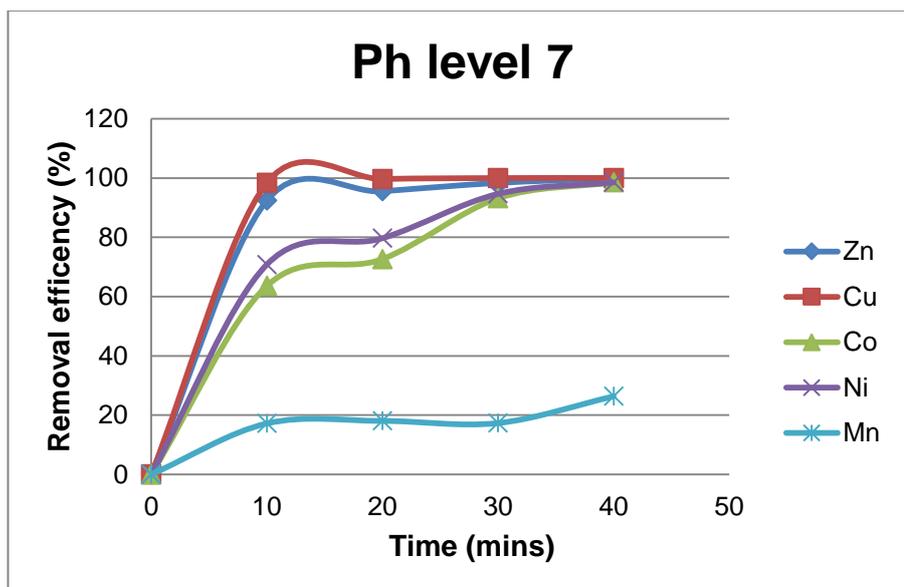


Figure 13 Metals removal at pH 7 at a current density 12.5mA/cm² and at an initial metal concentration of 50 mg/L

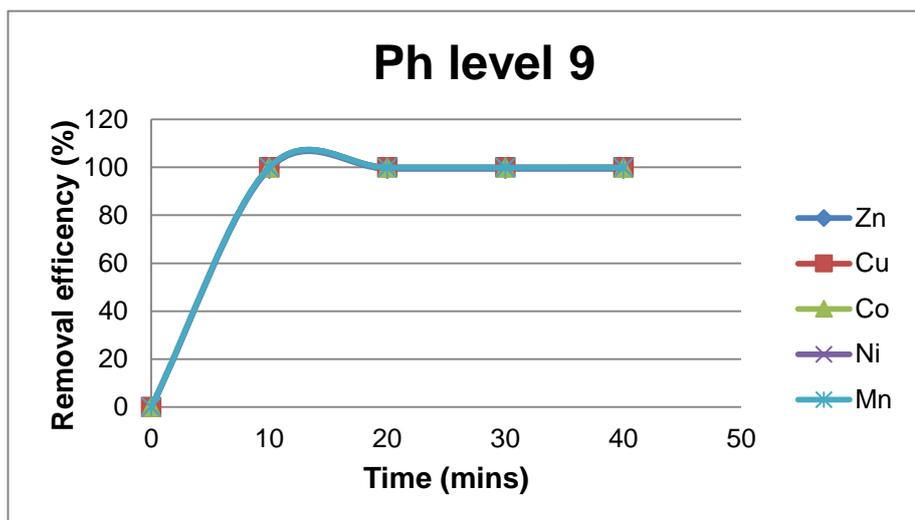


Figure 14 Metals removal at pH 9 at a current density 12.5mA/cm² and at an initial metal concentration of 50 mg/L

7.2 Effect of current density on removal rate

Since the best pH was observed to be 9 in first 3 tests, the effect of current density on removal was tested at an initial pH of 9 and at an initial metal concentration of 50mg/L. Current density is defined as the ratio of current passed in mA to area of electrode immersed, which was 40 cm². First, the current density of 6.25 mA/cm² was tested where 0.25 A was used at a voltage of 2.5 volts. Then, the change in removal was analysed by doubling the current passed for each of the next two experiments at the current of 0.5 A and 1 A at a voltage of 11 volts and 17 volts, respectively. The results are presented in the figure 15-17 below.

The results show that all the five heavy metals have removal efficiency of greater than 90% at the end of 10 minutes, with a removal efficiency reaching close to 100% for all heavy metals at the end of 20 minutes at all 3 current densities chosen for the experiments. It can be seen clearly from Figure 15, figure 16 and Figure 17 that all the current densities chosen for the experiments are more or less equally effective in removing the heavy metals. However, keeping the focus on the economical side of the electrocoagulation, it becomes essential to find out the electrical energy consumption of the experiment using the following equation.

$$E_c = \frac{V \cdot I \cdot t}{V_w},$$

where V is the voltage used in volts, I is the current passed in Amps, t is the electrolysis time and V_w is the volume of wastewater in m^3 . The electrical consumption, without compromising the removal efficiency was found to be at its lowest at a current density of 6.25 mA/cm^2 at the end of 20 minutes treatment. The individual calculations are not presented to prevent excessive longevity of the paper.

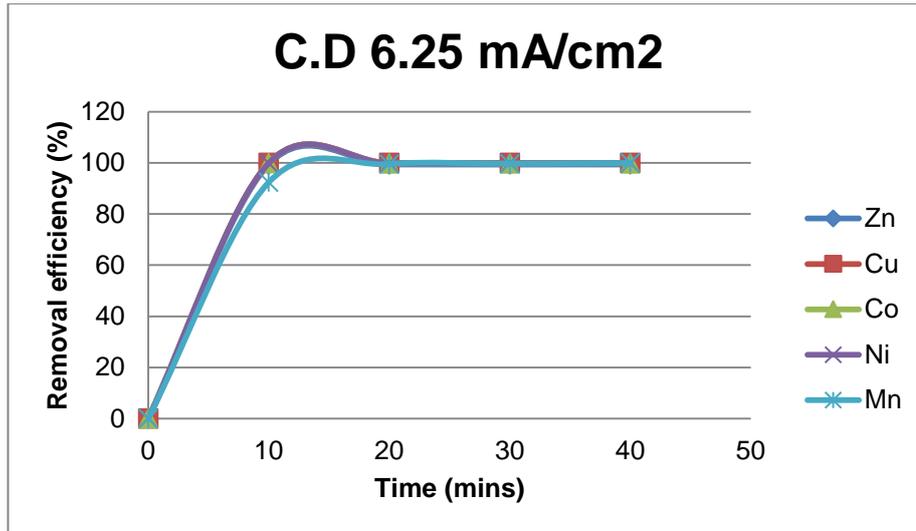


Figure 15 Metals removal at C.D of 6.25 mA/cm^2 , at pH9 and at an initial metal concentration of 50 mg/L

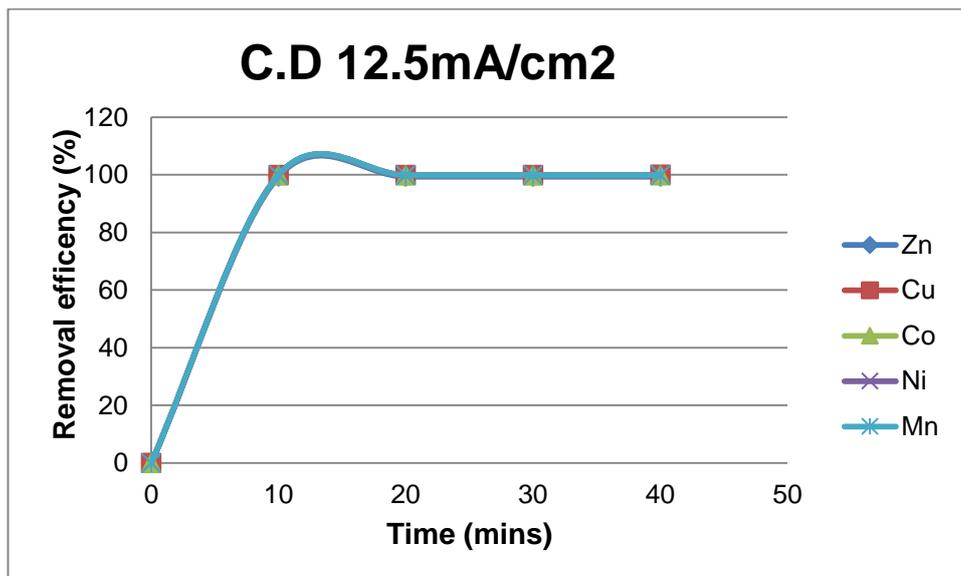


Figure 16 Metals removal at C.D of 12.5 mA/cm^2 , at pH9 and at an initial metal concentration of 50 mg/L

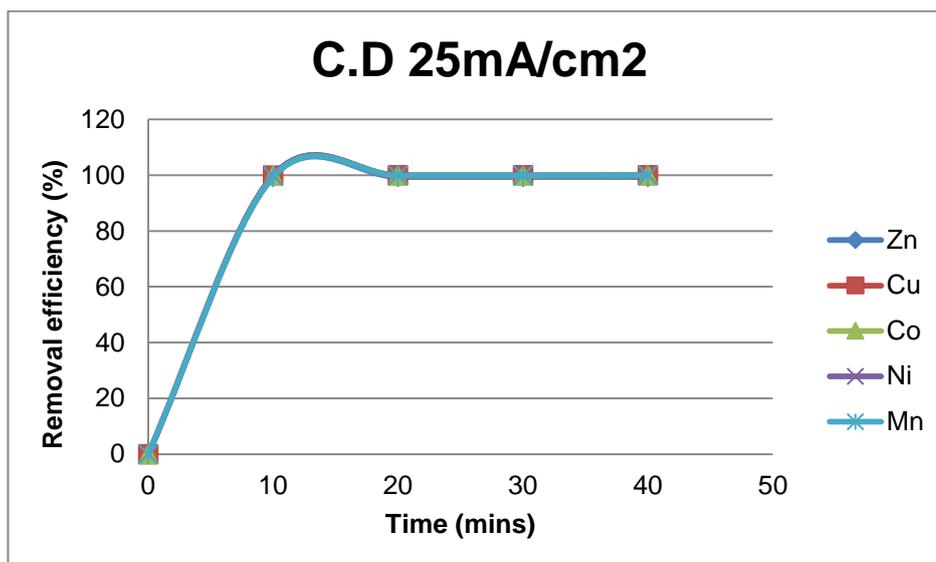


Figure 17 Metals removal at C.D of 25mA/cm², at pH9 and at an initial metal concentration of 50 mg/L

7.3 Effect of initial metal concentration

The effect of metal concentration on removal rate was examined using an increased metal concentration (50-150 mg/l) for all 5 heavy metals, and residual ion concentrations of metals were measured at different times. The experiments were performed using the constant pH level of 9 and the current density of 6.25 mA/cm² during all experiments.

The observed removal difference was very marginal but surprisingly, for the 3 heavy metals, Cu, Co and Ni, the removal efficiency improved slightly when the initial concentration increased from 50 to 100 mg/l. As seen from Figure 17 and Figure 18, the removal of zinc was not affected when increasing the concentration to 100 mg/l. Manganese was the only heavy metal whose removal rate was affected negatively when the concentration was increased. However, the removal of all 5 heavy metals was satisfactory at the end of 40 mins of experiment.

Removal rate was observed by further increasing the concentration to 150 mg/l for all heavy metals, the observed difference was again very marginal but all the 5 heavy metals showed a negative effect on removal rate when the concentration was increased to 150 mg/l with manganese being the least removed among all other metals in all the samples collected at different time intervals.

A removal rate of more than 99% was detected at the end of 40 minutes at all metal concentrations for the 4 metals excluding manganese.

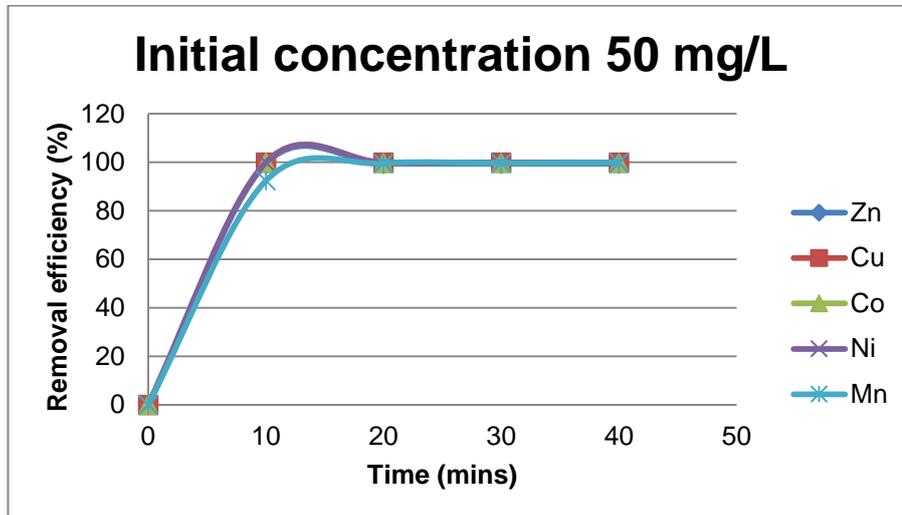


Figure 18 Metals removal at an initial concentration of 50mg/l, at a C.D of 6.25 mA/cm² and at a pH 9

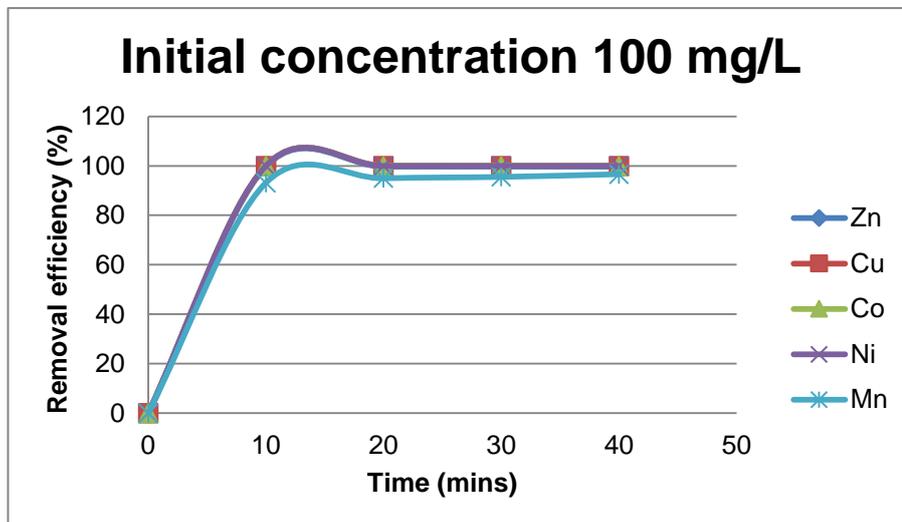


Figure 19 Metals removal at an initial concentration of 100mg/l, at a C.D of 6.25 mA/cm² and at a pH 9

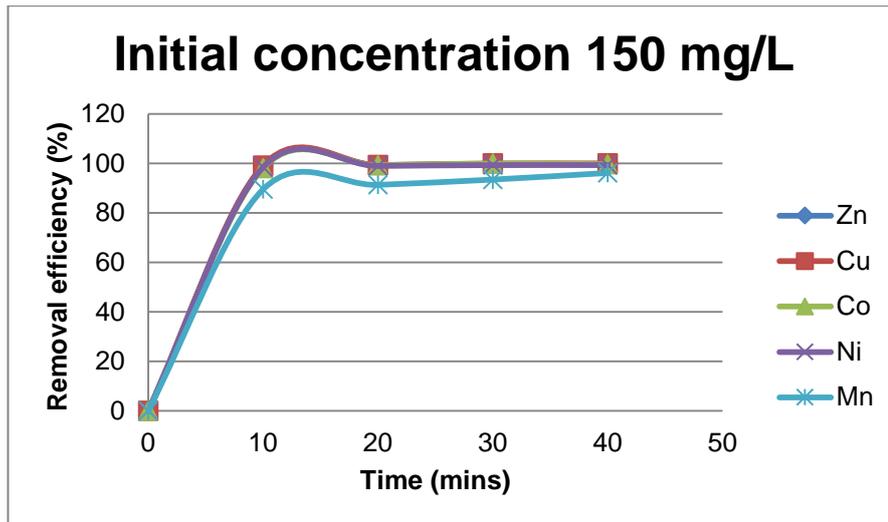


Figure 20 Metals removal at an initial concentration of 150mg/l, at a C.D of 6.25 mA/cm² and at a pH 9

7.4 Residual Iron analysis

Electrocoagulation when done with the iron electrodes, dissolve the iron ions into solution where they are later hydrolyzed to polymeric hydroxides followed by metal adsorption to formed iron hydroxides. Iron in drinking water is just as or more harmful than any other heavy metal. Hence, it became essential to know what amount of iron could be removed along with metals and what portion of iron would be left behind in the solution after the electrocoagulation.

Figure 21 below illustrates the residual iron in every sample taken at different time intervals of all 9 experiments performed at different parameter levels explained above. From the figure we can conclude that pH plays a significant role in the residual iron in the electrocoagulation. The first two experiments where the content of residual iron was at a substantial level were performed at pH 5 and pH 7; all the other experiments from 3 to 9 were performed at a high pH of 9 where the residual iron content is almost none at all time intervals. On Experiment 2 done at pH 7, the residual iron content surprisingly increased with time. One possible explanation for that can be the rate of Fe²⁺ ions, which are soluble in water, is more than the rate of oxidization to Fe³⁺ ions.

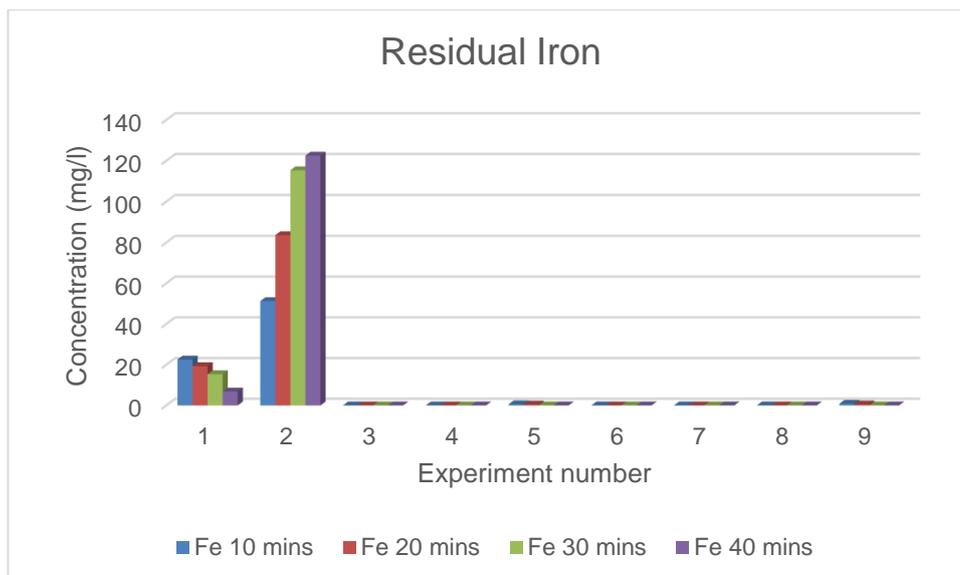


Figure 21 Chart displaying the residual iron after electrocoagulation in all 9 experiments

8 Conclusions

The aim of the thesis was to understand the mechanism of electrocoagulation in removing heavy metals from water and to assess the impact and optimize the different parameter levels associated with electrocoagulation in removal of heavy metals. The following conclusions could be drawn from the results of the experiments.

- Electrocoagulation can be used to remove the heavy metals from wastewater with great efficiency under right parameter levels. Among the chosen parameters for the experiments, the pH of 9, at the duration of 20 minutes were found to be the best among the chosen current densities of 6.25 - 25 mA/cm² and were enough to remove the heavy metals at all concentrations
- During electrocoagulation a significant increase in pH was observed possibly due to the production of hydroxide ions from the cathode. However, the pH decreased with time and was at the same initial level at the end of experiments.
- Electrocoagulation process is most efficient in removing heavy metals from wastewater at a high pH level of 9 possibly due to rapid oxidation of Fe²⁺ ions to Fe³⁺ ions, which otherwise are soluble. It could also be the reason why residual iron is at its lowest and almost none at pH 9.
- Manganese was the most resistant metal in reacting to electrocoagulation and only got removed to satisfactory levels at a high pH level of 9

- The Removal rate increased slightly with the increase in current density as Fe ions are produced at higher rate at high current density.

9 Limitations and Recommendations

Although the optimum parameter levels are presented in the conclusion part of the thesis the optimum level is only among the three chosen levels for all parameters. Hence, it is necessary to do more experiments at more levels. The importance of designing the experiment statistically was overlooked in this thesis and the experiments were performed with *one variable at a time* method which although gives an idea about the effect and optimization of variables chosen but cannot be trusted significantly. Hence the author proposes that the electrocoagulation experiments be performed in the future by using the concept and idea of statistics and by designing the experiment statistically.

Also other parameters that are influencing the electrocoagulation such as inter electrode distance, temperature, conductivity and electrode types were not chosen for the study in order to keep the number of experiments in control and were kept constant for all the experiments. The author also recommends studying the effect of these parameters by including them while designing the experiments. The author does not recommend that the electrocoagulation experiments be performed at low pH due to the possibility of forming soluble Fe^{2+} ions as a secondary contaminant unless steps such as pre oxidation by introducing an oxidant or by aerating the water to increase the dissolved oxygen content are taken to achieve rapid oxidation of Fe^{2+} ions at low pH.

The three chosen current densities for the experiments in the thesis were found to be very high and the removal of heavy metals was very rapid at even the lowest current density of 6.5 mA/cm^2 . Hence, the author also recommends that the electrocoagulation efficiency be tested by starting with the lower current densities.

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