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JUDUL: **DEGRADATION OF NICKEL FROM ELECTROPLATING WASTEWATER BY USING ULTRASONIC ASSISTED EXTRACTION IN ADDITION OF HCL**

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DEGRADATION OF NICKEL FROM ELECTROPLATING WASTEWATER BY USING ULTRASONIC ASSISTED EXTRACTION IN ADDITION OF HCL

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A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering

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NOVEMBER 2010

I declare that this thesis entitled “*Degradation of Nickel from Electroplating Wastewater by using Ultrasonic Assisted Extraction in Addition of HCl*” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

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To my beloved mother, *Rugayah binti Deraman*,
father, *Sudeerman bin Samsudin*

and

To my beloved brothers
Muhammad Fadhil bin Sudeerman
Muhammad Fuaad bin Sudeerman
Muhammad Farhan bin Sudeerman
Muhammad Fauzan bin Sudeerman

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ABSTRACT

Nickel is one of the heavy metals which are having a high relative atomic mass that can cause an environmental pollution and potential hazard to human health. The method currently practiced for the degradation of heavy metal is by using ultrasonic assisted extraction. Even in low concentration, heavy metal is considered as toxicity and imposes considerable risk on all forms because of their suspected carcinogenic properties. If hazardous compound spreading to environmental, high of energy is needed to treat it and leads to the high of cost operation. Other methods for degradation heavy metals take a longer extraction time. The degradation of nickel from electroplating wastewater was investigates by using 37 kHz ultrasonic cleaner and extraction assisted with solvent, HCl and without solvent. Experiments were carried out at concentration of solvent, HCl (1-3 mol/dm^3), sonication time (2-30 minutes), temperature (40-80^{o}C) and volume of solvent, HCl (1-15 mL). The comparison of nickel degradation with solvent and without solvent also has been studied. In presence of solvent, the percentage of nickel degradation was higher than without solvent. The higher percentage of nickel degradation was at 2.5 mol/dm^3 of solvent concentration (70.0 % nickel degraded), 20 minutes of sonication time without solvent (69.1 % nickel degraded) and with solvent (77.5 % nickel degraded), temperature was at 60^{o}C without solvent (67.7 % nickel degraded) and with solvent (75.5 % nickel degraded) and volume of solvent was at 2 mL (78.8 % nickel degraded). Finally, the result of the study showed that the nickel degradation increased with increasing solvent concentration, sonication time and temperature of degradation and decreasing volume of solvent. The best condition for all parameter applied was degraded 77.8 % of nickel.

ABSTRAK

Nikel adalah salah satu logam berat yang mempunyai jisim atom relatif tinggi yang boleh menyebabkan pencemaran alam sekitar dan berpotensi membahayakan kesihatan manusia. Kaedah yang dipraktikkan kini untuk degradasi logam berat adalah dengan menggunakan bantuan ekstraksi ultrasonik. Walaupun dalam kepekatan rendah, logam berat dianggap sebagai toksik dan terdedah risiko yang besar terhadap semua bentuk kerana sifat karsinogenik disyaki logam berat. Jika sebatian berbahaya menyebar ke persekitaran, tenaga yang tinggi diperlukan untuk merawat dan menyebabkan tingginya kos operasi. Kaedah lain untuk mendegradasi logam berat juga memakan masa pengekstrakan yang lebih lama Degradasi nikel dari air sisa elektrik penyepuhan dikaji dengan menggunakan 37 kHz pembersihan ultrasonik dan dibantu dengan ekstraksi pelarut, HCl dan tanpa pelarut. Kajian dilakukan pada kepekatan pelarut, HCl (1-3 mol/dm^3), masa sonikasi (2-30 minit), suhu (40-80^{o}C) dan isipadu pelarut, HCl (1-15 mL). Perbandingan degradasi nikel dengan pelarut dan tanpa pelarut juga telah dipelajari. Dengan kehadiran pelarut, peratusan penyingkiran nikel lebih tinggi daripada tanpa pelarut. Peratusan tinggi degradasi nikel sebanyak 2.5 mol/dm^3 kepekatan pelarut (70.0 % nikel terdegradasi), 20 minit dari masa sonikasi tanpa pelarut (69.1 % nikel terdegradasi) dan dengan pelarut (77.5 % nikel terdegradasi), suhu 60 ^{o}C tanpa pelarut (67.7 % nikel terdegradasi) dan dengan pelarut (75.5 % nikel terdegradasi) dan isipadu pelarut berada di 2 mL (78.8 % nikel terdegradasi). Akhirnya, hasil kajian menunjukkan bahawa penyingkiran nikel meningkat dengan meningkatnya kepekatan pelarut, masa sonikasi dan suhu degradasi dan penurunan isipadu pelarut. Keadaan terbaik dapat mendegradasi 77.8 % nikel

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LIST OF SYMBOLS/ABBREVIATIONS

Ni	-Nickel
Cd	-Cadmium
Zn	-Zinc
UAE	-Ultrasonic assisted extraction
Cr	-Chromium
Cu	-Copper
Mn	-Manganese
Pb	-Lead
Mg	-Magnesium
Co	-Cobalt
HCl	-Hydrochloric acid
$Ca(OH)_2$	-Calcium hydroxide
CO_2	-Carbon dioxide
$CaCO_3$	-Calcium carbonate
H_2O	-Water
$Al_2(SO_4)_3$	-Aluminium (III) sulphate
NaOH	-Sodium hydroxide
$Al(OH)_3$	-Aluminium (III) hydroxide
Na_2SO_4	-Sodium sulphate
m/v	-Mass per volume
M	-Molar, Concentration
^oC	-Degree Celcius
ME	-Maceration extraction

W	- Watt
^oF	-Degree Fahrenheit
HNO_3	-Nitric acid
min	-Minute
mL	-Mililitre
L	-Litre
%	-Percentage
mol/dm^3	-Mol per decimeter cube
AAS	-Atomic Absorption Spectrometer
mg/L	-Miligram per litre
OLFP	-Oligosaccharides longan fruit pericarp
kHz	-Kilohertz
V	-Volume, Voltan
t	-Time
T	-Temperature

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Wastewater from the electroplating industries has to be treated because it causes toxicity and foul odor to the water that can be a potential hazard to human health and the environment. The human activities that contaminate soil systems with the largest amounts of toxic metals can be found from the deposition of metal-rich mine tailing, metal smelting, leather tanning, electroplating, emissions from gas exhausts, energy and fuel production, down-wash from power lines, intensive agriculture, and sludge dumping (Marin *et al.*, 2001; Jeon and Yeom, 2006). Heavy metal is the one of the common and important hazardous chemical compounds in wastewater. The term of heavy metals is usually applied to common transition metals in the periodic table, such as nickel (Ni), cadmium (Cd), and zinc (Zn). These metals have a high relative atomic mass and can cause an environmental pollution (heavy-metal pollution) which are from a lead in petrol, industrial effluents, the smelting of copper and leaching of metal ions from the soil into lakes and rivers by acid rain. Heavy metals are also the main group of inorganic contaminants. Even though the concentration of heavy metal is low, it is considerable as toxicity. Heavy metals can affect the reproduction, survival, sex ratio and human development.

From nickel, it can affect the immune system, lung, skin (Mendez, 2002), dermatitis, nausea, chronic asthma, coughing and human carcinogen (Babel and Kurniawan, 2003). It is high solubility in water is the main reason why the degradation of these metals to acceptable levels is a relatively difficult process. A large area of land is contaminated with heavy metals due to use of sludge or municipal compost, pesticides, fertilizers, and emissions from municipal waste incinerators, car exhausts, residues from metalliferous mines, and smelting industries (Garbisu and Alkorta, 2003; Halim *et al*., 2003). Methods for heavy metal degradation are devided into two methods which are conventional and modern methods. It can be removed by chemical precipitation, ion exchange and electrochemical removal (Eccles, 1999), membrane filtration (Kurniawan *et al*., 2006), microwave assisted digestion (Filgueiras *et al*.,2000) and ultrasonic assisted extraction (Filgueiras *et al.*,2000; Vilkhu *et al*., 2008; De La Calle *et al*.,2009).

The method currently practiced in the industry for the degradation of heavy metal is by using ultrasonic assisted extraction. Sanchez *et al*. (1994) investigated the use of UAE for the analysis of the heavy metals such as Cd, Cr, Cu, Mn, Ni, Pb, and Zn in several European reference materials. The advantages of this method are that economically viable, safe to operate, can be used for both liquid and solid samples and for the extraction of either inorganic or organic compounds (Harper *et al*., 1983).

Nowadays, the application of ultrasonic in wastewater treatment has attracted great interest. It has been proposed as one of the alternative techniques for degradation of hazardous organic compounds. Ultrasonic technology as an innovative technology may be used for water and wastewater treatment for pollution removal. The basis for the present day generation of ultrasound was established as far back as 1880 with the discovery of the piezoelectric effect by the Curies (Gelate *et al*., 2000).

1.2 Problem Statement

Even in low concentration, heavy metal is considered as toxicity and improper handling of these metals or inadequate discharge of their wastes result in long-term deterioration of the water environment and imposes considerable risk on all forms because of their suspected carcinogenic properties. When hazardous compound spreading to environmental, more energy is needed to treat it resulting to high of energy consumption and it leads to the high of cost operation. When treating the hazardous compound from discharge of wastewater, energy that will be used is low and the cost of operation will be better than when it spread to the river which can cause pollutants.

There are several problem in terms of time consuming. By doing this research, ultrasonic assisted extraction will reduce the extraction time and can achieve the higher percentage of heavy metal degradation with the parameter such as concentration of solvent, sonication time and temperature.

1.3 Objective of Study

Based on the background of this study, the objective was to obtain the best conditions in nickel degradation from electroless nickel plating wastewater by using ultrasonic assisted extraction process in term of addition of hydrochloric acid, HCl.

1.4 Scope of Study

There are some important tasks to be carried out in order to achieve the objective of this study. The important scopes have been identified for this research in achieving the objective:

1.4.1 To compare the percentage of nickel degradation on ultrasonic process with HCl and without HCl.

1.4.2 To study the parameter that affects the percentage of heavy metal degradation using ultrasonic assisted extraction such as concentration of solvent, sonication time, temperature and volume of solvent.

1.5 Rationale and Significant of Research

1.5.1 Good laboratory practice in performing laboratory testing of ultrasonic assisted extraction method of nickel removal from electroplating industrial wastewater will be developed.

1.5.2 Reduce the energy consumption by treating from the discharge of wastewater rather than it release in environmental.

1.5.3 Benefit to society such as avoid health affection like central nervous system cause, immune system, lung, skin and asthma.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical processes of heavy metal degradation

There are a few conventional and modern methods of removing heavy metals. Table 2.1 was summarised the main advantages and disadvantages for the various methods of removing heavy metal that have been done in previous researches.

Table 2.1 The main advantages and disadvantages for various methods of removing heavy metal.

Method	Advantages	Disadvantages
Chemical precipitation	Low capital cost, simple operation	Sludge generation, extra operational for sludge disposal, incomplete removal and high-energy requirements
Adsorption	Low-cost, easy operating conditions, having wide pH range, high metal binding capacities	Low selectivity and production of waste products
Membrane filtration	Small space requirement, low pressure, high separation selectivity, low energy	High operational cost due to membrane fouling

Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption
Photocatalysis	Removal of metals and organic pollutant simultaneously and less harmful by-products	Long duration time, limited applications
Microwave assisted digestion	Ease of the operation	Long duration time
Ultrasonic assisted extraction	Used for both liquid and solid samples, for the extraction of inorganic or organic compounds, economical, ease and safe to operate, lower time consuming, lower temperature for higher yield.	

Heavy metal can be removed by chemical precipitation, ion exchange, electrochemical removal, adsorption, membrane filtration such as complexation-ultrafiltration, electrodialysis, photocatalysis, microwave assisted digestion and ultrasonic assisted extraction.

2.1.1 Chemical Precipitation

Chemical precipitation is the technology used to remove dissolved ionic metals from solutions, such as process wastewaters containing toxic metals. The ionic metals are converted to an insoluble form particle by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling or filtration. The unit operations typically required in this technology include neutralization, precipitation, coagulation or flocculation, solids or liquid separation and dewatering. The effectiveness of a chemical precipitation process is dependent on several factors, like the type and concentration of ionic metals present in solution, the precipitant used, the reaction conditions especially the pH of the solution, and the presence of other constituents that may inhibit the precipitation reaction. The widely used chemical precipitation process is hydroxide precipitation, in which metal hydroxides are formed by using calcium hydroxide, $Ca(OH)_2$ or sodium hydroxide, NaOH as the precipitant.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \textbf{(2.1.1a)}$$

$$Al_2(SO_4)_3 + 6\ NaOH \rightarrow 2\ Al(OH)_3 + 3\ Na_2SO_4 \quad \textbf{(2.1.1b)}$$

However, chemical precipitation method has several disadvantages to remove heavy metal which are sludge generation, extra operational for sludge disposal, incomplete removal and high-energy requirements (Kurniawan *et al*., 2006; Eccles, 1999).

2.1.2 Adsorption

Adsorption is present in many natural physical, biological, and chemical systems, and is used in industrial applications. Activated carbon, silica sand, alumina and coal are usually used as an adsorbent. The effectiveness of an adsorbent depends on the adsorptive properties of their surface. Adsorption is caused by attraction of Van der Waals force which exists between molecules. Adsorption process has advantages in term of low-cost operation, easy operating conditions, having wide pH range, high metal binding capacities, but this process has several disadvantages which is has low selectivity because of the forces acting on molecules are not really strong and production a lot of waste products (Babel and Kurniawan, 2003; Aklil *et al*.,2004)

2.1.3 Membrane Filtration

Membrane filtration is one of the methods used in industry to remove heavy metal. There are various types of membrane filtration such as ultrafiltration, microfiltration, nanofiltration and reverse osmosis. In membrane filtration, a solvent is passed through a semi-permeable membrane. The membrane's permeability is determined by the size of the pores in the membrane, and it will act as a barrier to particles which are larger than the pores, while the rest of the solvent can pass freely through the membrane. The result is a cleaned and filtered fluid on one side of the membrane, with the removed solute on the other side. These unique specialties enable membrane filtration to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (Vigneswaran *et al.*, 2004). Some significant findings were reported by Juang and Shiau (2000), who studied the removal of Cu(II) and Zn(II) ions from synthetic wastewater using chitosan-enhanced membrane filtration.

There are a few advantages of membrane filtration which are small space requirement, low pressure and high separation selectivity but it still have a major disadvantages in membrane filtration processes which is to realise a high permeate flux. For the case of ultrafiltration, the particles rejected by the membrane deposit on the membrane surface will form a cake layer. The consequence is an additional flow resistance and permeate flux through the membrane is decrease. This effect can be influenced by the filtration operation mode. The filtration resistance increases and the permeate flux through the membrane decreases with time (Melin and Rautenbach, 2003). It is also has a disadvantage in term of high operational cost due to membrane fouling (Kurniawan *et al.*, 2006).

2.1.4 Electrodialysis

Electrodialysis is a membrane separation in which ionized species in the solution was applying an electric potential to pass through an ion exchange membrane. The membranes are thin sheets of plastic materials with either cationic or anionic characteristics. When a solution containing ionic species passes through the cell compartments, the anions move toward the anode and the cations toward the cathode, crossing the anion exchange and cation exchange membranes (Chen, 2004). Electrodialysis has higher separation selectivity, but this method has disadvantages similar as membrane fitration method which is has higher operational cost due to membrane fouling and energy consumption (Mohammadi *et al*., 2005).

2.1.5 Photocatalysis

Photocatalytic process in aqueous suspension of semiconductor has received considerable attention in view of solar energy conversion. This photocatalytic process was achieved for rapid and efficient destruction of environmental pollutants. From the previous research, photocalysis process was used by Zhang and Itoh (2006) on titanium dioxide particle. This process has an advantages like can remove the metals and organic pollutant simultaneously and less harmful by product but it is still has a problems in term of long duration time and limited applications (Barakat *et al*., 2004; Kajitvichyanukula *et al*., 2005)

2.1.6 Microwave Assisted Digestion

Microwave assisted digestion is based on the direct application of electromagnetic radiation to a material such as organic solvent and plant tissue which has the ability to absorb electromagnetic energy or microwaves and to transform it into heat. It is also one of the methods used in industry to remove heavy metals. This method has advantages in term of ease to operate. However, it is still has disadvantages such as long duration time and dangerous when carried out the process because the use of concentrated acid. (Filgueiras *et al*., 2000)

2.1.7 Ultrasonic Assisted Extraction

Many technologies are used nowadays to treat large volumes of wastewater diluted metal ion-containing solution such as membrane filtration, ion exchange and adsorption. However, these processes are very expensive and require high level of expertise to operate and maintain the process. The common techniques currently practiced in the industry for the heavy metals removal are by microwave assisted digestion and ultrasonic assisted extraction because these both methods are ease to operate (Filguieras *et al*., 2000). However, ultrasonic assisted extraction was better than microwave assisted digestion in removing heavy metals.

One of the advantages of ultrasonic assisted extraction was in term of time consuming. Ultrasonic assisted extraction has a shorten time compared to microwave assisted digestion. Filgueiras *et al*. (2000) reported that the time needed for one extraction was approximately of 7 min where 3 min for sonication time and 4 min for separation of the extract. This time was much lower than acid digestion process which is 47 min where 7 min for acid digestion, 20 min with an ice bath for the reactor to cool before opening and 20 min for heating to dryness so that excess of acid can be eliminated. Ma *et al.* (2008) reported that the advantages of ultrasound assisted extraction, which can achieve at lower temperature and can efficiently reduce extraction time. Boonkird *et al.* (2008) stated that Capsaicinoid recovery by UAE was 3 hours compared maceration was 15 hours and Soxhlet was 5 hours From this result, it shows that ultrasonic-assisted extraction have an advantage in term of time for running the process.

Beside that, ultrasonic assisted extraction also have an advantages in term of safety when handling the process. Furthermore, the use of corrosive concentrated acids is avoided. The procedures are safer than acid digestion because of low pressure and temperature present during extraction procedure. The whole procedure is also simpler since a lesser number of operations is involved that will minimizes contamination risks. According to Hristozov *et al*. (2004), the ultrasound extraction procedure was reported to be a good alternative to the common microwave digestion since it is less hazardous because it works under atmospheric pressure and does not use a higher concentrated acid. It is also considerably cheaper than the microwave system. Lavilla *et al*. (1999) have a similar opinion where ultrasonic assisted extraction be an attractive alternative to microwave-assisted digestion such as avoiding concentrated acids, pressure reactions and time consumption involved. It shows that the cost of removal heavy metal from the sample is lower by using ultrasonic assisted extraction rather than microwave assisted digestion.

On the other side, ultrasonic assisted extraction also has an advantages in term of the quantity of solvent used to degrade heavy metals. In previous research, Rezic *et al.* (2008) was applied the small volume of organic solvent on historic textile to degrade heavy metals by using ultrasonic assisted extraction. As a results, the higher efficiency and faster in extraction are found from this research. It can be seen that the small volume also has an ability to degrade heavy metal. On the other hand, it is also economically because of the small solvent volume used. Beside that, the lower temperature also take as advantage of UAE where Boonkird *et al.* (2008) found that the higher degradation was available at the lower operational temperature for UAE compared to a conventional industrial hot maceration process. It shows that UAE also has an advantage in term of temperature.

Ultrasonic-assisted extraction is commonly used for the heavy metals removal from sample. The other samples like sewage sludge (Hristozov *et al.*, 2004) and waste oils (Fontana *et al.*, 1996) also can be extracted by this process. From the previous researches, there are a lot of parameter that effect the percentage of heavy metals degradation have been studied by using ultrasonic assisted extraction method such as effect of solvent concentration, sonication time, temperature, volume of solvent (Filgueiras *et al.*, 2000; Deng *et al.*, 2009)

2.2 Influence of solvent concentration

Function of solvent for the ultrasonic assisted extraction extraction process is much important. Deng *et al.* (2009) mentioned that the extraction efficiency was improved when ultrasound was used to assist acid in extracting heavy metals. Acid used as a solvent. Ultrasounic generated synergy with acid treatment, and the synergistic effect became greater with increasing concentrations of acid (solvent). It is means that ultrasound alone was not effective enough to extract most of the heavy metals from the sample. From their research, it can be seen that increases in solvent concentration, the percentage of degradation also increases and by addition of solvent, the percentage of degradation also higher compared to without addition of solvent.

Filgueiras *et al*. (2000) stated that the concentration of the acid as solvent was the most critical parameter affecting ultrasonic-assisted extraction. Extraction efficiency increases with increasing acid concentration until a steady extraction efficiency being reached. From their previous research, hydrocloric acid was chosen for extraction since it has not oxidant properties and also being more convenient than nitric acid. Rezic *et al*. (2008) found that the use of hydrochloric acid, HCl gaves a higher percentage degradation of nickel from the historic textile.

2.3 Influence of sonication time

Filgueiras et al. studied the three metals which are magnesium, manganese and zinc for the effect of sonication time toward the extraction efficiency. As a result, extraction efficiency increased with increasing sonication time from 1 to 2 min. Extraction efficiency was slightly worse when the temperature of the medium exceeded 50–60 °C, which occurred after a 3 min sonication time. A sonication time of 3 min was seen to be suitable for metal extraction.

In another research, Deng *et al*.(2009) found that the heavy metal contents in the supernatant increased with increasing sonication time either by addition of solvent or without. For untreated sludge, the increases were low at less than 5 min and became more rapid with increases in sonication time. The soluble heavy metal contents were higher in addition of solvent compared to without addition of solvent.

From both researches, the sonication time also dependent on the sample used. Filgueiras *et al*. (2000) used a plant while Deng *et al*. (2009) used sewage sludge as a sample, respectively. The sample with higher viscosity and more concentrated, the sonication time for the sample to achieve the optimum condition will be increase. The increases in sonication time, the percentage of degradation also increase until the optimum condition was achieved.

2.4. Influence of temperature

According to Zhang *et al*. (2008), in the UAE, the yield of flaxseed oil was found to decrease with the increase of temperature. The yield of flaxseed oil was about 83 % at 30 ^{o}C and decreased by 6 % to about 77 % at 50 ^{o}C. Finally, 30 ^{o}C or room temperature may be seen as an optimum condition for the extraction of flaxseed oil in UAE.

According to Hristozov *et al*. (2004) used ultrasound-assisted extraction was studied as sample preparation method for inductively coupled plasma optical emission spectrometry analysis of eight metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in sewage sludge. The optimum condition for temperature was 90 ^{o}C. From their research, they found that increase in temperature, the percentage degradation was increases.

Temperature also has a relationship with sonication time. Temperature of the extraction medium increase with increasing of sonication time. Usually, when the temperature increases up to 50 ^{o}C, extraction efficiency is increased as a result of the larger number of cavitation nucleus formed (Lorimer and Mason, 1987; Agranat *et al*., 1987). As the temperature approaches the boiling point of the liquid, ineffective sonication occurs as a result of the decrease in surface tension and increase in vapor pressure within the microbubble, which in turn cause the damping of the shock wave (Mason *et al*., 1989)

In observation, degradation of heavy metal will increase as the temperature increase, but further increase after achieved the optimum condition, no significant change occur. It is maybe cause from the boiling point of the mixture or sample used. High temperature is not beneficial for ultrasonic extraction because of evaporation of solvent (Ma *et al.*, 2008).

2.5 Influence of volume of solvent

Filgueiras *et al.* (2000) have been studied about influence of solvent to percentage of degradation. They used volume of solvent in the range of 3 mL to 9 mL. From this research, they found that 5 mL was the optimum condition. In another research, Hristozov *et al.* (2004) reported that used of 10 mL acid mixture which is 5 mL of HCl and 5 mL of HNO_3 gives the optimum volume of solvent for the sewage sludge sample. From both researches, it can be conclude that usually small quantity of solvent used in UAE.

2.6 Ultrasonic theory

Figure 2.1 shows the ultrasonic mechanism usually applied for degradation of heavy metals and cleaning process.

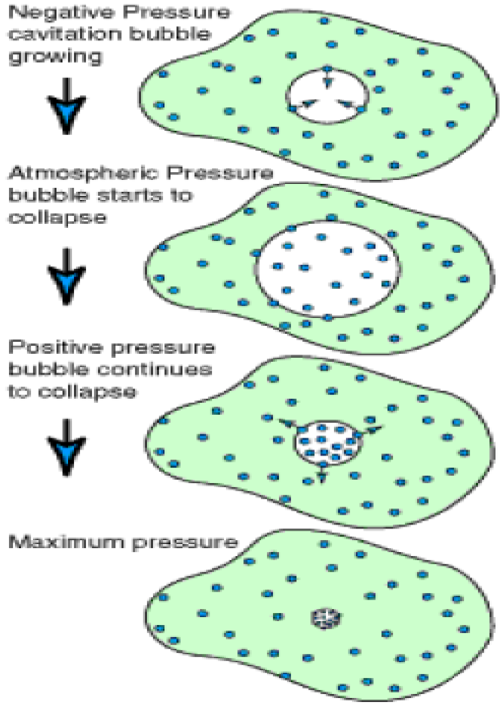


Figure 2.1 Ultrasonic mechanism (John Fuchs F., 2002)

Ultrasonic is sound transmitted at frequencies above the range of human hearing. An ultrasonic cleaner consists of an ultrasound generator along with transducer mounted on the bottom of a liquid-filled ultrasonic bath. The generator and transducer create alternating waves of compression and expansion in the liquid at extremely high speeds. Ultrasonic energy is generated by a piezoelectric transducer which is powered by a generator. Tranducer is used to converting alternating electrical energy to vibratory mechanical energy.

When sonicating liquids at high intensities, the sound waves that propagate into the liquid medium result in alternating compression (high-pressure) and rarefaction (low-pressure) cycles, where the rates depending on the frequency. During the rarefaction, high-intensity ultrasonic waves create small bubbles in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a compression resulting in the propagation of microscopic shock waves. This phenomenon is called as cavitation. Cavitations phenomenon was first identified and reported in 1895 (Thornycroft and Sydney, 1895). Shock waves from cavitation in liquid-solid slurries produce high velocity-inter particle collisions, the impact of which is sufficient to melt most metals (Pesic 1996). Thus the ultrasonic energy may be effective to remove the sorbed contaminants, like heavy metals.

CHAPTER 3

METHODOLOGY

3.1 Chemical and Apparatus used

During the research, few chemical and apparatus are used to complete the research process. The chemical and apparatus use are as following:
List of glassware and apparatus used is shown in Table 3.1.

Table 3.1: List of glassware and apparatus

Apparatus
Conical flask 100 mL
Measuring cylinder 10 mL, 50 mL, 100 mL
Volumetric flask 2 L, 100 mL
Glass rod
Beaker 50mL, 100 mL
Vials 30 mL
Dropper

List of chemical and reagents used is shown in Table 3.2.

Table 3.2: List of chemical and reagents

Chemicals	**Purity**	**Supplier**	**Purpose of Use**
Wastewater	-	VS Metal Finishing Sdn. Bhd.	As a raw material in this research.
Hydrochloric acid (HCl)	37 % fuming	Merck, Darmstadt, Germany	As a solvent in ultrasonic process.
Nickel solution	1000 mg/ L	Merck, Darmstadt, Germany	As a standard solution.
Nitric acid (HNO_3)	AAS grade	-	As a solvent in AAS equipment.
Distilled Water	-	-	To prepare a standard solution.

The equipments used in this study is shown in Table 3.3.

Table 3.3: List of equipments

Equipment	**Model**	**Frequency**	**Power/ Voltan**	**Purpose of Use**
Ultrasonic Cleaner	S-60 Elmasonic, Germany	37kHz	220V	To degrade nickel
Atomic Absorption Spectrometer	Z-5000 Polarized Zoeman Atomic Absorption Spectrophotometer Hitachi	-	-	To analyze nickel to get the absorbance and concentration

3.2 The Overall Methodology

The experimental procedures can be divided by into two parts:

1. Preparation of nickel calibration curve
2. Preparation of nickel degradation

3.2.1 Preparation of Nickel Calibration Curve

Calibration curve or standard is one of the methods used to determine the unknown concentration of sample by comparing the unknown concentration with a standard sample of known concentration. Atomic Absorption Spectrometer (AAS) will come out with the result of absorbance and concentration of unknown sample. Therefore, both initial and final concentrations of wastewater sample can be known.

Standard solution was prepared by dilution of standard 1000 mg/L nickel solution into range of 30 mg/L until 40 mg/L. About 4 standard solutions of nickel at different known concentration were added with one drop of nitric acid, HNO_3 before enter the AAS equipment for concentration determination. The sample of unknown concentration also goes to the same step.

3.2.2 Preparation of Nickel Degradation

The aim of this experiment was to study the degradation of nickel from electroless nickel plating wastewater which involves the use of hydrochloric acid as a solvent. The experiment was carried out with constant volume of wastewater which is 100 mL. Then, wastewater will be irradiated with ultrasonic frequency where fixed to 37 kHz. These processes are divided by four parameters which are solvent concentration, sonication time, temperature and volume of solvent. The methods are repeated at all study effects. For effect of sonication time, the range of time used is between 2 min to 30 min, the experiment was carried out at constant temperature which is 70 ^{o}C. For effect of temperature, the temperature of ultrasonic cleaner was set up and varies from 40 ^{o}C to 80 ^{o}C and sonication time of higher degradation of nickel degradation get it from first parameter is used which is 20 min.

The above methods were repeated for all parameter effect and the experiment was proceeding by adding HCl as a solvent into wastewater sample. For effect of the solvent concentration, the range of concentration used is between 1.0 mol/dm^3 to 3.0 mol/dm^3 at constant temperature and sonication time which is 70 ^{o}C and 20 min, respectively. The last parameter which is volume of hydrochloric acid added, the volume used in the range of 1 mL until 15 mL and solvent concentration, sonication time and temperature of higher percentage of nickel degradation get from first, second and third parameter were used which is 2.5 mol/dm^3, 60 ^{o}C and 20 min, respectively. The study effect was to achieve the higher of nickel degradation. Lastly, the result obtained was compare between the percentage of nickel degradation by adding HCl and without adding HCl.

3.3 Experimental Analysis

After wastewater sample solution was degrading by ultrasonic process for 2 minutes until 20 min, the sample was taken out from ultrasonic cleaner. After that, the sample solution was filtered using filter pump and then one drop of nitric acid, HNO_3 was added to the sample solution before measured with Atomic Absorption Spectrometer, AAS to get the unknown concentration of the sample solution.

The above methods were repeated for the different sample of study effects. The result data from AAS was come out with absorbance and concentration of the sample.

Therefore, the final concentration of unknown sample solution can be known. From there, the percentage of nickel degradation also can be determined by using Equation 3.1.

$$\textbf{\% degradation} = \frac{\textbf{Initial Concentration} - \textbf{Final Concentration}}{\textbf{Initial Concentration}} \times 100 \tag{3.1}$$

where Initial Concentration (mg/L)
Final Concentration (mg/L)

All the method process was summarized in the figure below;

Figure 3.1 is shown about the preparation of nickel degradation by using ultrasonic process without addition of solvent, HCl and Figure 3.2 is shown about the preparation of nickel degradation by using ultrasonic assisted extraction with addition of solvent, HCl.

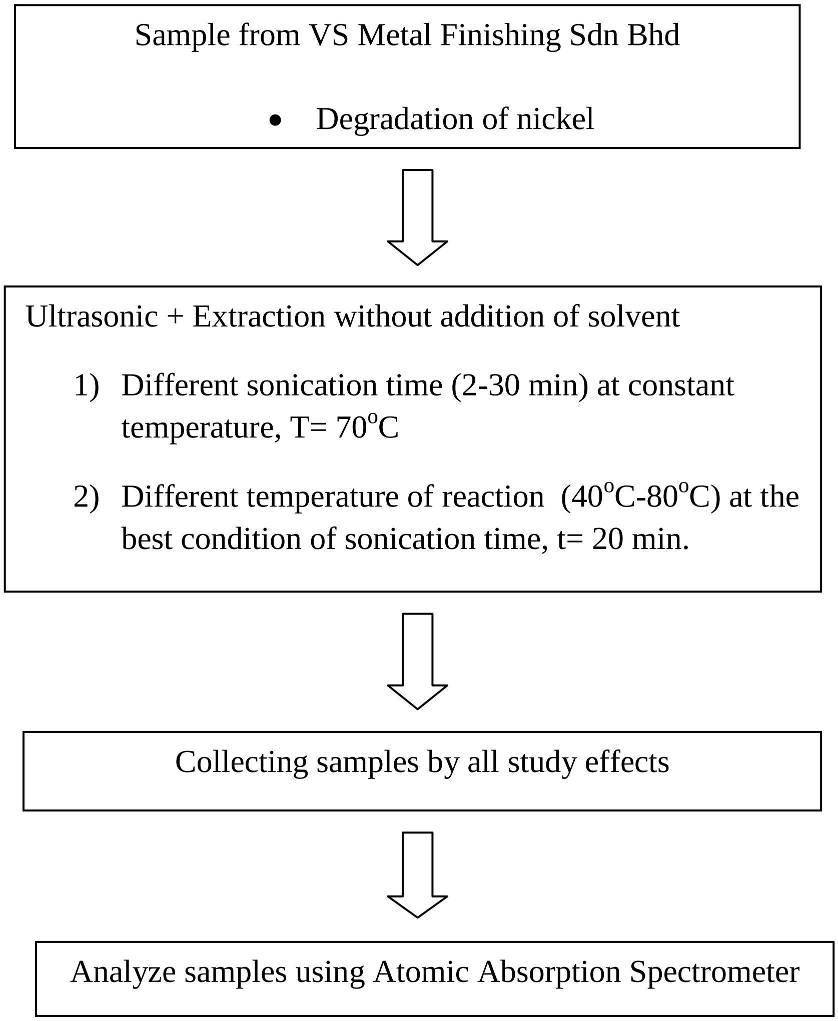
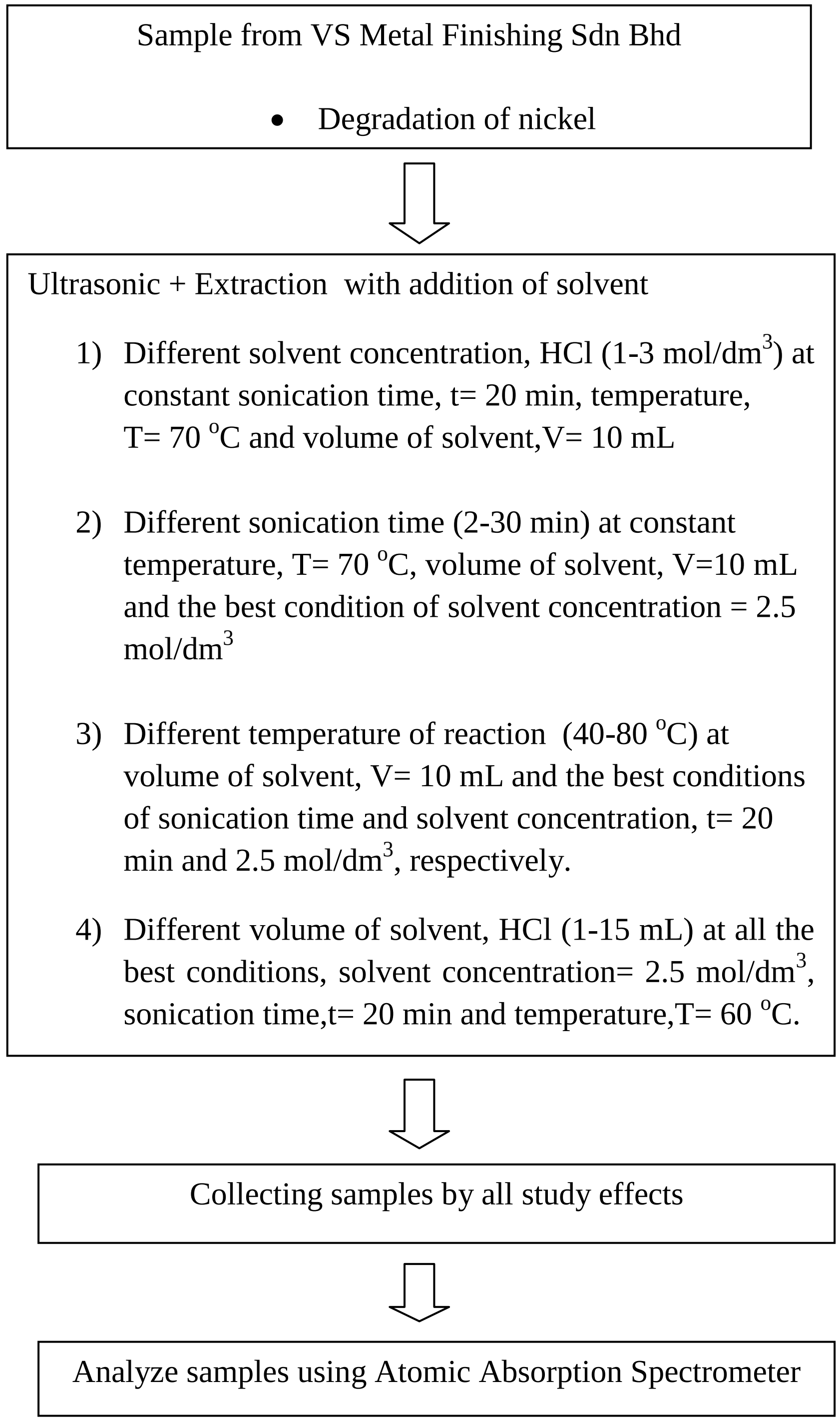


Figure 3.1 Preparation of nickel degradation by using ultrasonic assisted extraction process without addition of solvent, HCl



Sample from VS Metal Finishing Sdn Bhd

- Degradation of nickel

Ultrasonic + Extraction with addition of solvent

1) Different solvent concentration, HCl (1-3 mol/dm^3) at constant sonication time, t= 20 min, temperature, T= 70 ^{o}C and volume of solvent,V= 10 mL
2) Different sonication time (2-30 min) at constant temperature, T= 70 ^{o}C, volume of solvent, V=10 mL and the best condition of solvent concentration = 2.5 mol/dm^3
3) Different temperature of reaction (40-80 ^{o}C) at volume of solvent, V= 10 mL and the best conditions of sonication time and solvent concentration, t= 20 min and 2.5 mol/dm^3, respectively.
4) Different volume of solvent, HCl (1-15 mL) at all the best conditions, solvent concentration= 2.5 mol/dm^3, sonication time,t= 20 min and temperature,T= 60 ^{o}C.

Collecting samples by all study effects

Analyze samples using Atomic Absorption Spectrometer

Figure 3.2 Preparation of nickel degradation by using ultrasonic assisted extraction process with addition of solvent, HCl

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of solvent concentration

Figure 4.1 shows the percentage of degradation for different solvent concentrations (HCl) in the range of 1 mol/dm^3 to 3 mol/dm^3 for sonication time at 20 min and temperature at 70 ^{o}C.

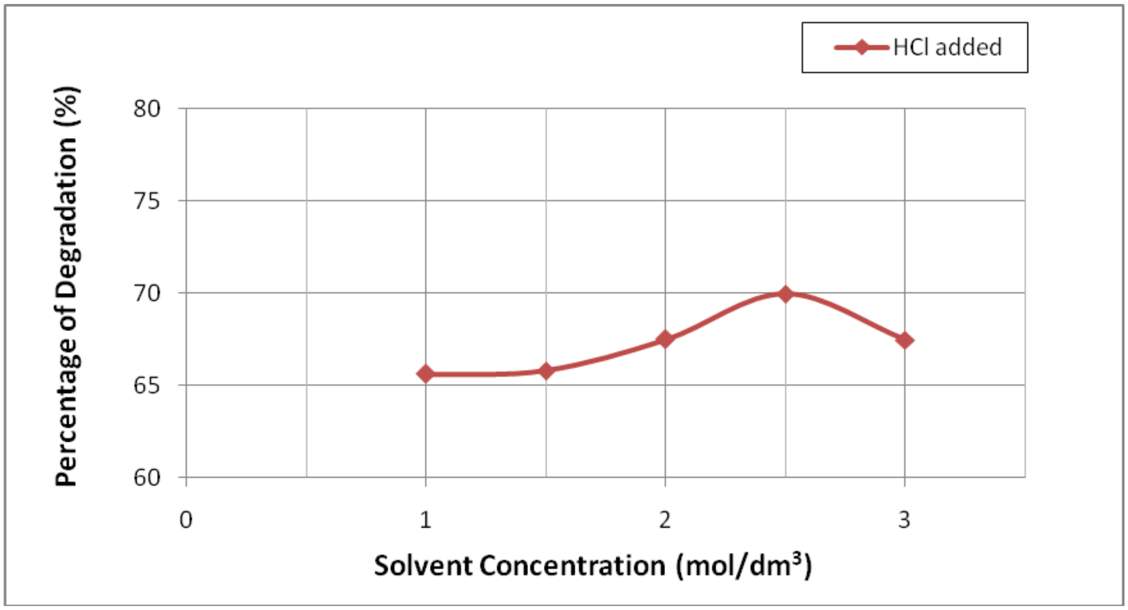


Figure 4.1 Effect of Solvent Concentration (HCl) on the Percentage of Degradation (conditions: volume sample: 100 mL; volume solvent: 10 mL; solvent concentration: 1 – 3 mol/dm^3; sonication time: 20 min and temperature: 70 °C)

The effect of solvent concentrations on the nickel degradation was carried out for sonication time at 20 min and temperature at 70 °C. It was found that with increasing solvent concentration, the percentage of nickel degradation also was increased until the best condition of solvent concentration was achieved. The further increases of solvent concentration, percentage of nickel degradation were decreases. It can be seen from the Figure 4.1 where at initial solvent concentration 1 mol/dm^3, the percentage of nickel degradation was 65.6 % and generally increases with increasing solvent concentration; 1.5 mol/dm^3 (65.8 %); 2.0 mol/dm^3 (67.5 %); 2.5 mol/dm^3 (70.0 %) and 3.0 mol/dm^3 (67.5 %). Therefore, the best condition of solvent concentration was 2.5 mol/dm^3.

From this results, when ions (H^+ and Cl^-) is added into solution, it exerts an intermolecular force which binds loosely to the water molecules in solution. This weak force then increases the energy necessary to break each molecule loose. However, further increases in solvent concentration to the solution after the highest percentage of nickel degradation was achieved, the viscocity of the solution become greater. Therefore, cavitation effect will become lower and decrease in vapor pressure within the microbubble. As a result, more than 2.5 mol/dm^3 HCl no longer become effective to nickel degradation.

Beside that, ultrasonic cleaner avoid to used a large number of concentrated acid (Filgueiras *et al*., 2000). This means that at the too higher concentration of solvent, it is become ineffective. It is one of the reason why the percentage of nickel degradation reduced from 2.5 mol/dm^3 to 3.0 mol/dm^3.

The result obtained followed closely to the previous research. Deng *et al*. (2009) used nitric acid as a solvent in their research. The soluble heavy metal contents increased with increasing nitric acid concentration whether or not ultrasound was applied. The optimum solvent concentration was 0.325 M in the range of 0.0065 M to 0.65 M. However, further increases in nitric acid concentration led to only a slight increase in the extraction of heavy metals. From their research, solvent was the key important parameter in term of concentration for heavy metal removal.

Filgueiras *et al.* (2000) reported that acid concentration in the liquid extractant was seen to be the most critical parameter affecting ultrasonic assisted extraction. From their work, hydrochloric acid, nitric acid and a mixture of hydrochloric acid and nitric acid were used as a solvent. Extraction efficiency which is heavy metal degradation was increase as a solvent concentration increases.

Hydrochloric acid was chosen as a solvent since it has not oxidant properties and being more convenient than acid nitric (Filgueiras *et al.*, 2000). The term of ‘not oxidant’ properties or ‘anti-oxidant’ properties means a chemical compound that readily transfers oxygen atoms or a substance that gains electrons in a redox chemical reaction. Hristozov *et al*. (2004) used hydrochloric acid, nitric acid and a mixture of hydrochloric acid and nitric acid which is the same type of solvents as Filgueiras *et al.* (2000). From this research, the use of pure nitric acid gives much lower recoveries. Rezic *et al*. (2008) used hydrochloric in their research and found that by using this solvent, the higher degradation of nickel was obtained.

4.2 Effect of sonication time

Figure 4.2 shows the percentage of degradation for different sonication time in the range of 2 min to 30 min, with and without the addition of solvent (HCl) for constant solvent concentration (HCl) at 2.5 mol/dm^3 and temperature at 70 ^{o}C.

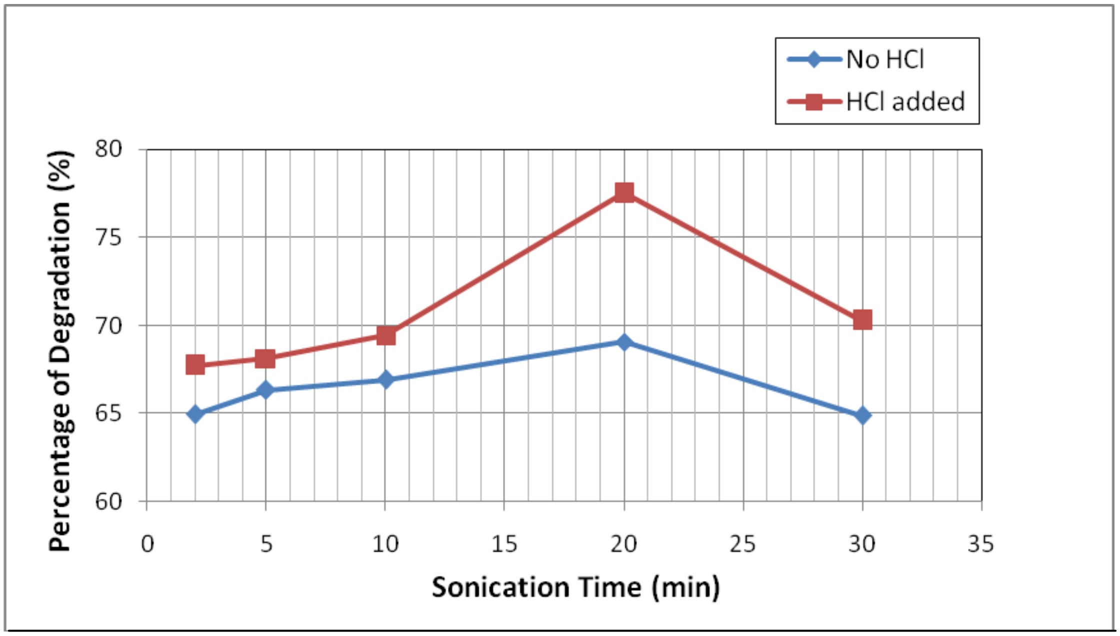


Figure 4.2 Effect of Sonication Time with and without the Addition of Solvent (HCl) on the Percentage of Degradation (conditions: volume sample: 100 mL; volume solvent: 10 mL; sonication time: 2 min to 30 min; solvent concentration: 2.5 mol/dm^3 and temperature: 70 ^{o}C)

As reported by previous workers, the length of time used in sonication was important (Davidson and Delevoye, 2001). The effect of sonication time on the nickel degradation was carried out for sonication time in the range of 2 min to 30 min where solvent concentration was at 2.5 mol/dm^3 and temperature at 70 ^{o}C. It was found that with increasing sonication time, the percentage of nickel degradation also was increased until the optimum sonication time was achieved. The further increases of sonication time, percentage of nickel degradation were decreases. This observation was applied to both with and without the addition of solvent (HCl). It can be seen from the Figure 4.2

above where at initial sonication time without the addition of solvent (HCl) which is 2 min, the percentage of nickel degradation was 64.9 % and generally increases with increasing sonication time; 5 min (66.3 %); 10 min (66.9 %); 20 min (69.0 %) and 30 min (64.9 %).

The method above was repeated by adding 10 mL of 2.5 mol/dm^3 solvent (HCl) into the 100 mL of wastewater sample solution under the similar intervals of sonication time which is 2 min to 30 min and at the constant temperature, 70 ^{o}C. From the graph in Figure 4.2, it can be seen that after adding HCl solvent, the percentage of nickel degradation was increases compared to without addition of solvent (HCl). The result obtained for initial sonication time which is 2 min, the percentage of nickel degradation was 67.7 % and also generally increases with increasing sonication time until the optimum condition was reached; 5 min (68.1 %); 10 min (69.4 %); 20 min (77.5 %) and 30 min (70.3 %). From the result, the best condition of sonication time was at 20 minutes.

From this results, it can be conclude that the use of solvent influenced the percentage of nickel degradation. By addition of solvent, the percentage of nickel degradation was slightly higher compared to without addition of solvent. From 2 min to 20 min, the percentage of nickel was increased for both conditions. It is maybe because of the temperature of medium was too higher where the cavitation effect is maximized at approximately 160 ^{o}F or 71.1 ^{o}C for pure water. Sonication time also have a relationship with temperature where at higher temperature usually as the temperature increases up to 50 °C, extraction efficiency is increased as a result of the larger number of cavitation formed. As the temperature approaches the boiling point of the liquid, ineffective sonication occurs. Therefore, surface tension will be decrease and increase in vapor pressure within the microbubble, which in turn cause the damping of the shock wave. As a result, the percentage of nickel degradation was decrease in the range of 20 min to 30 min.

There are a few previous researches that are used effect of temperature as a parameter and slightly similar to this result. Hristozov *et al*. (2004) used the temperature range between 10 min to 50 min for degradation of heavy metals from sewage sludge samples. In their research, it can be seen that the observation of percentage of degradation was increases when sonication time was increases until it reach the optimum point. The optimum point was at 20 min. In the other research, the range of temperature between 1 min to 20 min used by Deng *et al*. (2009). The heavy metal removal was increased with increasing sonication time whether or not the sludge was extracted by 0.065 M nitric acid, HNO_3. In their research, the optimum temperature also was achieved at 20 min by 0.065 M nitric acid assisted by ultrasonic. The extension of sonication time may facilitate to extract more heavy metals from sludge, but it still have negative effects such as higher energy consumption and stronger break up of sludge floc structures that caused more difficulty in dewaterability (Feng *et al.*, 2009).

4.3 Effect of Temperature

Figure 4.3 shows the percentage of degradation for different temperature in the range between 40 ^{o}C to 80 ^{o}C, with and without the addition of solvent (HCl) for constant solvent concentration (HCl) at 2.5 mol/dm^{3} and sonication time at 20 min.

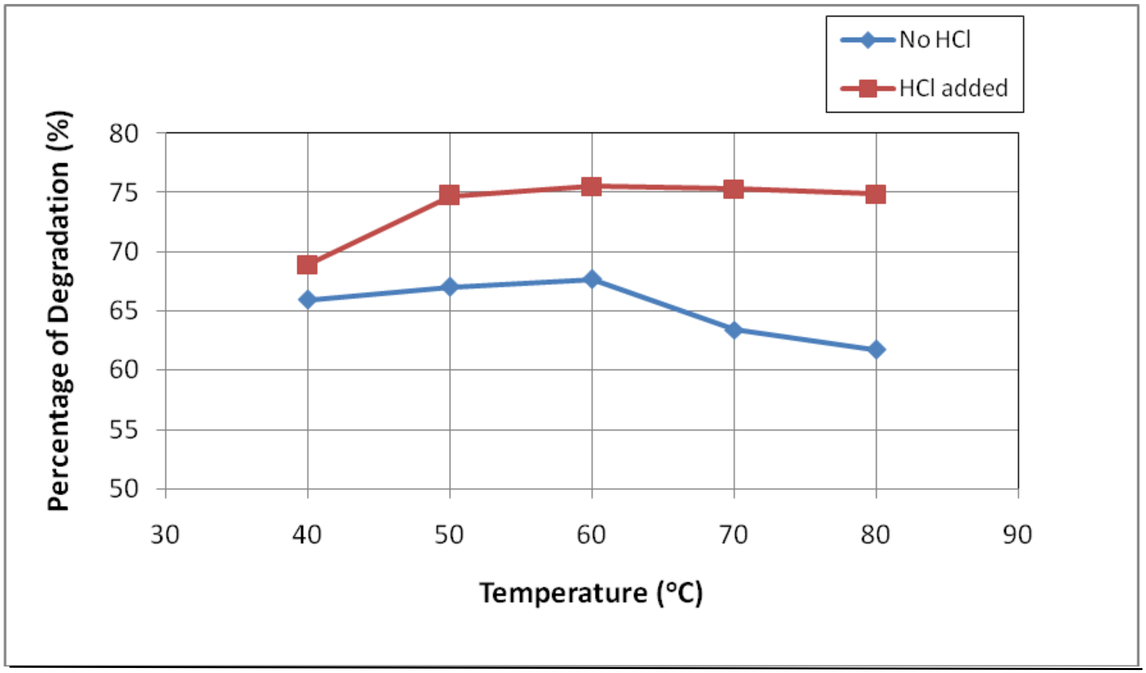


Figure 4.3 Effect of Temperature with and without the Addition of Solvent (HCl) on the Percentage of Degradation (conditions: volume sample: 100 mL; volume solvent: 10 mL; temperature: 40 ^{o}C – 80 ^{o}C; sonication time: 20 min and solvent concentration: 2.5 mol/dm^{3})

The effect of temperature was carried out for the temperature in the range between 40 ^{o}C to 80 ^{o}C at 2.5 mol/dm^{3} of solvent concentration, 20 min of sonication time and 10 mL of volume of solvent, HCl. From the observation, the percentage of nickel degradation with addition of solvent was higher compared to without addition of solvent, HCl.

From the graph in Figure 4.3, it can be seen that after adding HCl solvent, The result obtained for initial temperature which is 40 ^{o}C, the percentage of nickel degradation was 68.9 % and also generally increases with increasing sonication time until the best condition was reached; 50 ^{o}C (74.7 %); 60 ^{o}C (75.5 %); 70 ^{o}C (75.3 %) and 80 ^{o}C (75.0 %). For the without addition of solvent, the result obtained for initial temperature which is 40^{o}C, the percentage of nickel degradation was 65.9 % and also generally increases with increasing sonication time until the best condition was reached; 50 ^{o}C (67.1 %) and 60 ^{o}C (67.7 %). However, the further increases in temperature, the percentage of nickel degradation was decreased which is 70 ^{o}C (63.4 %) and 80 ^{o}C (61.7 %).

It can be conclude that in the addition of solvent, HCl, the percentage was increases as a temperature increases until the best condition was reached. The further increases of temperature after the best condition, the percentage of degradation has no significant change. The result for without addition of solvent, the temperature was also increases until the best condition reached, but for the further increases of temperature, the percentage of degradation was decreases. The best condition of temperature was decided at 60 ^{o}C for both with and without addition of solvent, HCl.

The result obtained was slightly similar to the previous researches that have been done. Jiang et al. stated that a positive relationship was found between ultrasonic temperature and OLFP recovery (Jiang *et al*., 2009). The OLFP recovery increased with the increase of ultrasonic temperature, especially when the temperature fell within the range of 40 ^{o}C to 70 ^{o}C. However, OLFP recovery decreased with increasing ultrasonic temperature because of high ultrasonic power. It is generally accepted that increasing ultrasonic temperature reduces liquid viscosity and density, and consequently increases mass transfer (Hemwimol *et al*, 2006). Furthermore, high ultrasonic temperature leads to the increase of cavitation bubble number and surface contact area (Palma and Barroso, 2002). Therefore, an appropriately high ultrasonic temperature can enhance extraction efficiency.

By using ultrasonic assisted extraction (UAE), extraction process enable at lower temperatures, According to Xu *et al*. (2000), both of them have compared UAE with hot water extraction of flavonoids from bamboo leaves. From the laboratory scale trials results showed that the optimum conditions for extraction were achieved using UAE at lower temperature, rather than using hot water bath extraction at 80 °C.

The addition of solvent, HCl into the wastewater sample solution also was related to the surface tension of the solution where the ionic forces that affect the equilibrium of the bond were introduced. Therefore, as the hydrogen bonds between the water molecules are disrupted, the surface tensions of the water will decrease making the collapse of cavitation bubbles more frequently and faster to occur (Neil Kensington, 1941). Surface tension in dependent on temperature where increasing the temperature with addition of solvent, HCl, surface tension will decreasing and influence to the higher degradation of nickel.

4.4 Effect of volume of solvent, HCl

Figure 4.4 shows the percentage of degradation for different volume of solvent, HCl in the range between 1 mL to 15 mL, for constant solvent concentration (HCl) at 2.5 mol/dm^3, sonication time at 20 min and temperature at 60 ^{o}C.

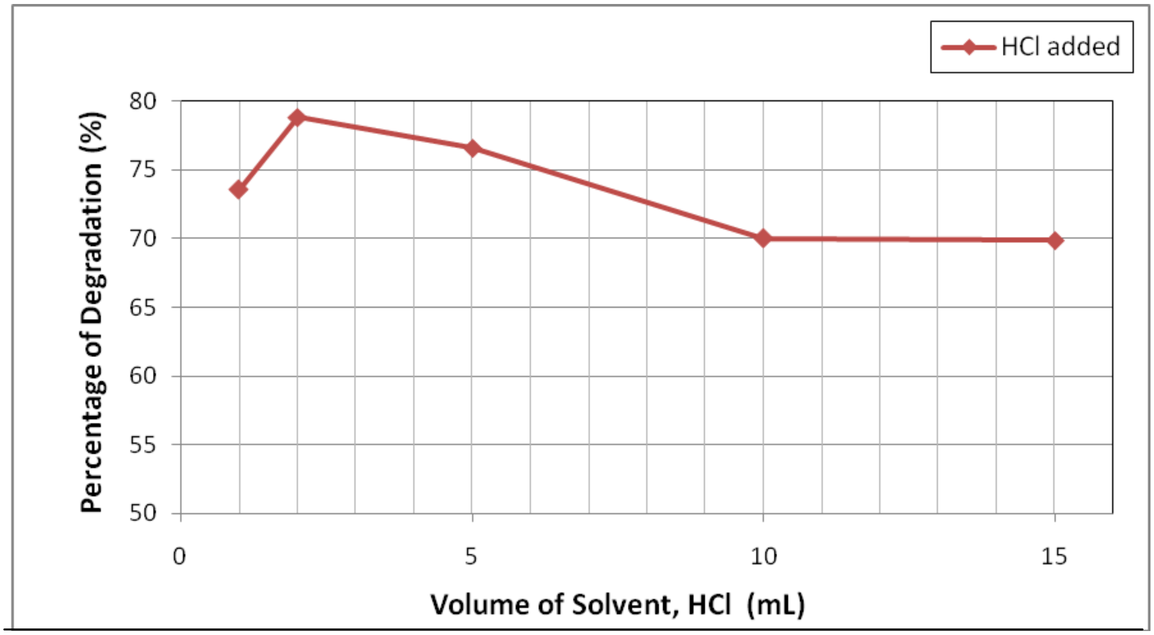


Figure 4.4 Effect of solvent of volume, HCl on the Percentage of Degradation (conditions: volume sample: 100 mL; volume of solvent, HCl (1 mL to 15 mL); temperature: 60 ^{o}C; sonication time: 20 min and solvent concentration 2.5 mol/dm^3)

The objective of this research was to compare the degradation by using solvent and without using solvent. The influence of the addition of HCl as a solvent on the degradation of nickel was carried out for study effects of sonication time and temperature. The results are shown in comparison by both study effects and it was observed that nickel degradation have a high percentage degradation with presence of solvent compared to the absent of solvent.

The result obtained for effect of volume of solvent, HCl was shown in Figure 4.4 above. The effect of volume of solvent, HCl was carried out in the range of 1 mL to 15 mL. It can be seen that the percentage of degradation was increases from 1 mL to 2 mL, and then volume of solvent between 2 mL to 10 mL was decreases. However, a further increase in volume of solvent until 15 mL was has no significant changes; 1 mL (73.5 % nickel degraded), 2 mL (78.8 % nickel degraded), 5 mL (76.6 % nickel degraded), 10 mL (70.0 % nickel degraded) and 15 mL (69.9 % nickel degraded). Therefore, the best condition for volume of solvent, HCl was 2 mL.

From this result, the volume of solvent used was small to achieve the higher percentage of nickel degradation. It is because by using the larger volume of solvent, the viscosity of solution become higher and the vapor pressure will decreases. Therefore the attraction forces no longer stronger to attract between the molecules. The higher volume of solvent become ineffective to degrade nickel.

There are a few result obtained from the previous researches about effect of volume of solvent on percentage of degradation that have been done. Rezic *et al.* (2008) was applied the small volume of organic solvent on historic textile to degrade heavy metals by using ultrasonic assisted extraction. As results, the higher efficiency and faster in extraction are found from this research. It can be seen that the small volume also has an ability to degrade heavy metal. According to Filgueiras *et al.* (2000), volume of solvent, HCl in the range of 3 mL to 9 mL was studied in their research. The optimum volume of solvent obtained was 5 mL. Hristozov *et al.* (2004) reported that used of 10 mL acid mixture which is 5 mL of HCl and 5 mL of HNO_3 gives the optimum volume of solvent for the sewage sludge sample. It was conclude that by using solvent with a small quantity was gives a higher percentage of degradation. It is also can operate with a low cost because the use of small quantity of solvent.

CHAPTER 5

CONCLUSION

5.1 Conclusion

Ultrasonic is widely used in various industries such as electroplating industrial. The used of ultrasonic assisted extraction has many advantages compared to other methods. This method also environmental friendly because has no poluttion impact to environment. As a conclusion, the degradation of nickel from electroplating industrial wastewater was investigated by using ultrasonic assisted extraction for several of operating conditions. The effects of parameters on nickel degradation were discussed and found that the percentage of nickel degradation was strongly dependent on the concentration of solvent used, sonication time, temperature and volume of solvent used. In this research also shows that use of solvent like hydrochloric acid, HCl can increase the percentage of phenol degradation effectively. The higher percentage of nickel degradation was found at 2.5 mol/dm^3 of solvent concentration where 70.0 % of nickel degraded and sonication time was at 20 min for both with and without solvent where 77.5 % and 69.1 % of nickel degraded, respectively. The best condition for temperature was at 60 ^{o}C for both with and without solvent where 75.5 % and 67.7 % of nickel degraded, respectively while for volume of solvent was at 2 mL where 78.8 % nickel degraded. Finally, the result showed that the nickel degradation increased with increasing solvent concentration, sonication time and temperature and decreasing volume of solvent. The best condition for all parameters applied was degraded 77.8 % of nickel.

5.2 Recommendation

Based on the observation from this research, there are a few recommendations was suggested to improve the percentage of nickel degradation. In order to get the best results, the other parameter can be considered for highly degradation of nickel such as ultrasonic amplitude, frequency, power and magnetic stirring time and speed.

Beside that, the use of both ultrasonic bath and ultrasonic probe also can be suggested. It is because by using both ultrasonics, the percentage of degradation will be higher rather than use of ultrasonic bath alone.

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APPENDIX A

THE EQUIPMENT USED DURING THE RESEARCH

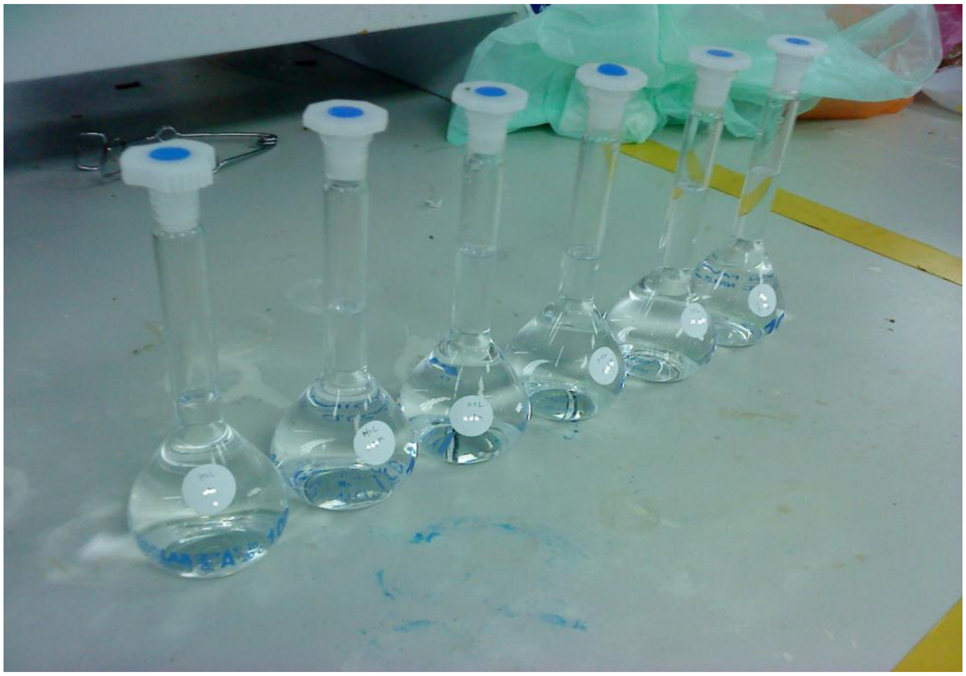
Appendix A.1 Ultrasonic Cleaner

Appendix A.2 Atomic Absorption Spectrometer (AAS)

APPENDIX B

CHEMICAL AND REAGENT USED DURING THE RESEARCH

Appendix B.1 Sample from electroplating wastewater



Appendix B.2 Hydrochloric acid with different concentration

APPENDIX C
CALCULATION FOR PREPARING NICKEL STANDARD SOLUTION

Preparing for nickel standard solution

Concentration of nickel standard solution: 1000 mg/L

Concentration of nickel standard solution needed:

30 mg/L, 33 mg/L, 37 mg/L and 40 mg/L

By using the dilution formula;

$M1V1 = M2V2$

Solution volume = 100mL

For 30 mg/L,

(1000 mg/L) ($V1$) = (30 mg/L) (100 mL)

$V1$ = 3.0 mL

For 33 mg/L,

(1000 mg/L) ($V1$) = (33 mg/L) (100 mL)

$V1$ = 3.3 mL

For 30mg/L,

(1000 mg/L) ($V1$) = (37 mg/L) (100 mL)

$V1$ = 3.7 mL

For 40mg/L,

(1000 mg/L) ($V1$) = (40 mg/L) (100 mL)

$V1$ = 4.0 mL

- Nickel standard solution (1000 mg/L) volume needed:
  (3.0 + 3.3 + 3.7 + 4.0) mL = **14 mL**

APPENDIX D

CALCULATION FOR PREPARING HCL CONCENTRATION

Calculation molarity of HCl from purity given;

Known: 36.5 gram-molecular weight HCl

: 37.0 % purity

: 1.191 = specific gravity relative to H_2O

Therefore;

0.37 x 1.191= 0.44067 (unitless)

0.44067 x 1 g/mL = 0.44067 g/mL = y molarity

0.44067 g/mL = 440.67 g in one liter

- (440.67 total g/L)/(36.5 gram-molecular weight HCl)
- = 12.07 M

The solvent concentration, HCl needed:

1.0 M, 1.5 M, 2.0 M, 2.5 M and 3.0 M

By using the dilution formula;

M1V1 = M2V2

Solution volume = 100mL

For 1.0 M,

(12.07 M) (*V1*) = (1.0 M) (100 mL)

V1 = 8.285 mL

For 1.5 M,

(12.07 M) (*V1*) = (1.5 M) (100 mL)

V1 = 12.428 mL

For 2.0 M,

$(12.07\ M)\ (\ V1\ ) = (2.0\ M)\ (100\ mL)$

$V1 = 16.57\ mL$

For 2.5 M,

$(12.07\ M)\ (\ V1\ ) = (2.5\ M)\ (100\ mL)$

$V1 = 20.713\ mL$

For 3.0 M,

$(12.07\ M)\ (\ V1\ ) = (3.0\ M)\ (100\ mL)$

$V1 = 24.855\ mL$

- Hydrochloric acid, HCl solution (37.0% purity @ 12.07 M) volume needed:
  (8.285 + 12.428 + 16.57 + 20.713 + 24.855) mL = **82.851 mL**

APPENDIX E

RESULT DATA

Table E.1 Data for Effect of Solvent Concentration

Solvent Concentration, (mol/dm^3)	Initial Concentration, (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
1.0	53.62	18.44	65.614	T= 70^{o}C, t= 20 min
1.5		18.33	65.819	
2.0		17.43	67.497	
2.5		16.10	69.978	
3.0		17.45	67.460	

Table E.2 Data for Effect of Sonication Time

Solvent, HCl added				
Sonication Time, (min)	Initial Concentration, (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
2	58.18	18.77	67.735	M= 2.5 mol/dm^3, T= 70^{o}C
5		18.54	68.130	
10		17.78	69.436	
20		13.08	77.514	
30		17.30	70.261	

No solvent, HCl added				
Sonication Time, (min)	Initial Concentration, (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
2	53.62	18.80	64.942	T= 70^{o}C
5		18.05	66.341	
10		17.74	66.919	
20		16.58	69.082	
30		18.84	64.868	

Table E.3 Data for Effect of Temperature

Solvent, HCl added				
Temperature, (^oC)	Initial Concentration (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
40	56.32	17.50	68.931	M= 2.5 mol/dm^3, t= 20 min
50		14.23	74.737	
60		13.78	75.536	
70		13.90	75.323	
80		14.14	74.897	

No solvent, HCl added				
Temperature, (^oC)	Initial Concentration, (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
40	48.65	16.57	65.940	t= 20 min
50		16.03	67.050	
60		15.73	67.667	
70		17.81	63.392	
80		18.63	61.706	

Table E.4 Data for Effect of Volume of solvent

Volume of solvent, HCl (mL)	Initial Concentration (mg/L)	Final Concentration, (mg/L)	Percentage of degradation (%)	Constant Parameter
1	60.00	15.88	73.53	M= 2.5 mol/dm^3, t= 20 min, T= 60^{o}C
2		12.70	78.83	
5		14.05	76.58	
10		18.01	69.98	
15		18.07	69.88	