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

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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.

A**BSTRAK**

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
^{o}F	-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.

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

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

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