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**Master of Science  
Environmental Engineering**

**Ultrasound Assisted Oxone Activation by Nano Zero Valent Iron  
for Remediation of Cyanide and Total Petroleum Hydrocarbons  
in Industrial Wastewater**

**The Graduate School  
of the University of Ulsan**

**Department of Civil and Environmental Engineering**

**Ultrasound Assisted Oxone Activation by Nano Zero Valent Iron  
for Remediation of Cyanide and Total Petroleum Hydrocarbons  
in Industrial Wastewater**

**Supervisor: Byeong-Kyu Lee**

**A Dissertation**

**Submitted to  
The Graduate School of the University of Ulsan in Partial  
Fulfillment of the Requirements for the Degree of  
Master of Environmental Engineering**

**by  
Arif Qureshi Ubaidullah**

**Department of Civil and Environmental Engineering  
University of Ulsan, Korea  
April, 2020**

**ULTRASOUND ASSISTED OXONE ACTIVATION BY NANO  
ZERO VALENT IRON FOR REMEDIATION OF CYANIDE AND  
TOTAL PETROLEUM HYDROCARBONS IN INDUSTRIAL  
WASTEWATER**

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**SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF MASTER OF SCIENCE  
IN  
ENVIRONMENTAL ENGINEERING  
UNIVERSITY OF ULSAN**

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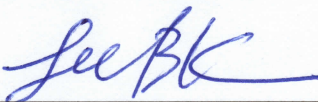
  
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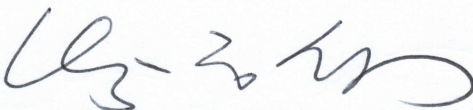
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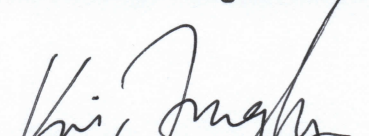
  
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Arif Qureshi Ubaidullah

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## **DEDICATION**

I would like to dedicate this thesis to my beloved daughter, parents and parents-in-law who taught me patience, love, and being loyal.

## ABSTRACT

Aqueous free cyanide is defined as the sum of the cyanide present as either hydrogen cyanide (HCN) or its deprotonated form, the cyanide anion ( $\text{CN}^-$ ), and is regarded as most acute toxic kind. Cyanide, as a chemical compound, can be found in the effluents of numerous industries, particularly mining, and refinery operations. The toxicity and concentration control of cyanide during industrial process and precious metal extractions necessitate the precise detection, determination and treatment of this compound. Therefore, this topic has been of prime focus for control and treatment of cyanide wastewater matrices.

In the theoretical part, numerous cyanide treatments have been compared and a new method of cyanide wastewater remediation via nano-zero valent iron (n-ZVI) and Oxone is proposed along with their chemistry and working mechanism. Later, the system thermodynamics, cyanide speciation with nZVI and free cyanide analysis technique as per developed standards is also discussed. In the experimental part, two set of water matrices (i.e. cyanide in DI water and polluted water) have been treated, analyzed and compared. Refinery tailings from a confidential company in South Korea with a free cyanide concentration of 12 ppm has been analyzed and investigated in this study. The current methodology being used at refinery complex to destroy cyanide is by means of alkaline chlorination, in which cyanide is converted into cyanate and is further oxidized into carbon dioxide and nitrogen. This tiresome process in terms of process economics, stringent process variables (such as pH) and low selectivity for cyanide among other hydrocarbon species is however replaceable. Since cyanide possesses extremely high affinity for metals thus nZVI was employed for the cyanide removal. The nZVI is corroded under sonication conditions in the presence of Oxone and yields ferrous ions ( $\text{Fe}^{+2}$ ). These ferrous ions ( $\text{Fe}^{+2}$ ) makes an insoluble ferro-cyano complex as soon as they encounter free cyanide.

Best results have been obtained at a nZVI catalyst loading of 0.3 mg/l and slightly lower pH (5.5 to 6.5). And a cyanide removal efficiency of 99% from refinery tailings has been successfully achieved.

*Keywords:* Cyanide Speciation, n-ZVI, Oxone, Free Cyanide, Speciation/Pourbaix diagram

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## CHAPTER 1

### 1.1 INTRODUCTION

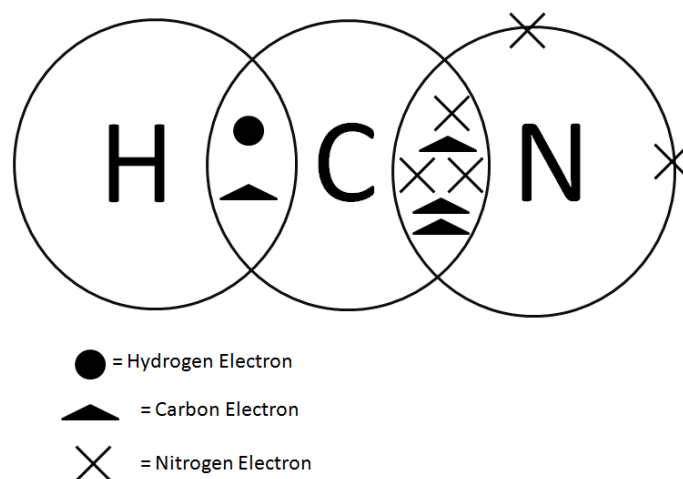
Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have a negative effect on the earth's environment [1]. Cyanide (as HCN or CN<sup>-</sup>, represented inclusively as CN) being one of them is an acute toxin & a highly reactive anion, which possess a diverse family of compounds. As a matter of fact, cyanide is ubiquitous, it is also found in some foods (e.g. bitter almonds, cassava etc.) [2].

It has been used for commercial purposes for over a century now and have a deep historical background. Cyanide (as free, organic or metal complexed cyanide compounds) finds its applications not only in mining, but also in cosmetics, pharmaceutical, food processing, plastics production, adhesives, surface finishing activities, leachate gasification, metal processing & smelting, petroleum refining, fire retardants, runoff road contacting salt and as an anti-caking agent. With its numerous benefits these sources also brings great risk to life and environment [3, 4]. Cyanide was used as a poison for centuries until the chemical was identified in 1782, when the Swedish pharmacist and chemist Carl Wilhelm Scheele isolated cyanide by heating the dye Prussian Blue with dilute sulfuric acid, obtaining a flammable gas (hydrogen cyanide) that was water soluble and acidic. Scheele called this new acid Berlin blue acid, which later became known as prussic acid and today is known as cyanide (from the Greek word "kyanos" meaning "blue") [2, 5]. Although there are many known forms of cyanide, but sodium cyanide is most commonly found in the environment, followed by potassium cyanide and gaseous hydrogen cyanide (later being only found in the air environment).

With such vast use of cyanide in industrial process, it also brings a serious threat to human, plant and aquatic life. Therefore, the water and other fluids being discharged into the environment must through a stringent check. And in order to achieve such rigorous wastewater discharge standards and regulations it is imperative to devise such a strategy so as to nullify the effect of the contaminants. Several methods for cyanide destruction, recovery or even complexation with other compounds have been discussed herein. More focus and light have been shed on cyanide wastewater complexation by oxidation of nZVI under sonication.

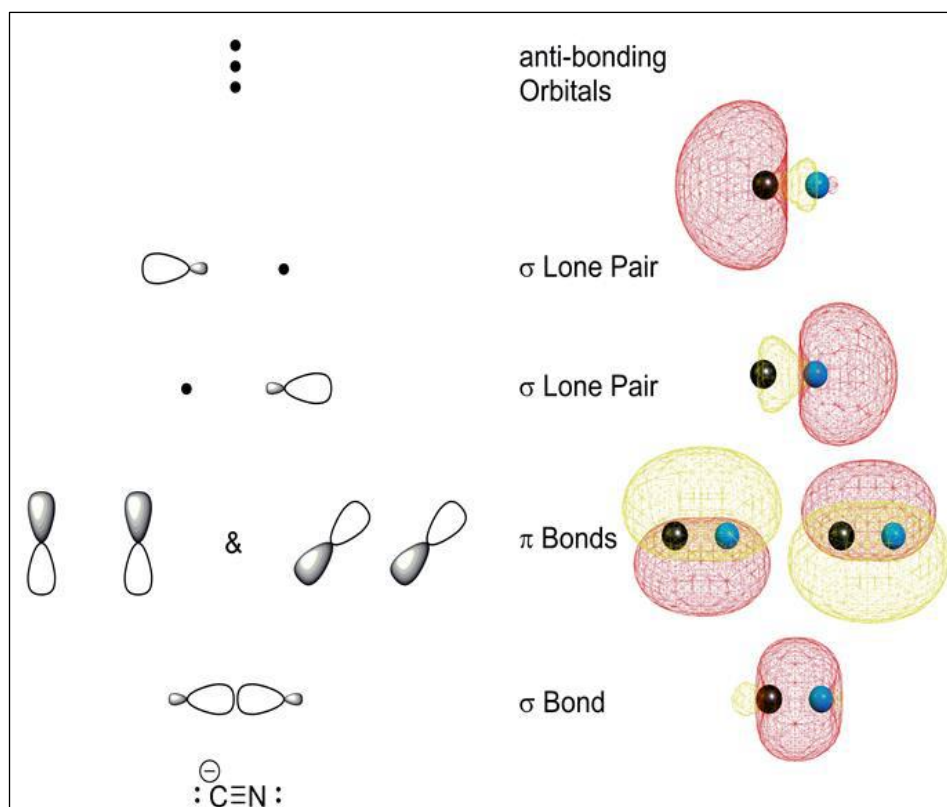
## 1.2 CYANIDE

The term “cyanide” refers to the wide variety of chemical compounds, all of which contain CN moiety in their structure [6]. Among all these chemical forms, free cyanide (sum of HCN and CN-) is the primary toxic agent, regardless of its source [7]. The chemical structure of CN- in which one atom of carbon is bonded to one atom of nitrogen through a triple bond is shown in figure 2 [8].



*Figure 1. The chemical structure of cyanide ion [8].*

The CN- structure shows that nitrogen has three bonds and one unshared pair of the electron. Although, carbon has the same structure, its tendency to form four bonds makes CN- unstable and highly reactive [9]. The Lewis structure of CN- in figure 3 represents one sigma ( $\sigma$ ) bond, two pi ( $\pi$ ), and two empty bonding orbitals. The s and p orbitals of this ion are filled with electrons and this makes cyanide behave similarly to a halogen (Pseudo-halogen behavior). The empty anti-bonding orbitals in this ion can form the bond with the d orbital of the transient metals which results in the formation of metal-cyanide compounds [10].



*Figure 2. The Lewis structure of cyanide ion [9].*

### 1.3 CYANIDE CLASSIFICATION

Metal cyanide complexes are classified in two main categories, weak metal cyanide complexes and strong metal cyanide complexes, based on the strength of the bonding between cyanide anion and metal cation. The relative stability and toxicity of cyanide compounds depends upon how easily they can release the cyanide anion ( $\text{CN}^-$ ) and requires moderate to high acidic pH conditions to dissociate in environment [11]. For instance, cyanide possess a very high affinity for metals, e.g. ferric ion ( $\text{Fe}^{3+}$ ), and low affinity for alkali earth metals, therefore simple cyanide salts like sodium and potassium cyanide brings serious risk to the environment. Contrarily, the complexes of cyanide with metals are very stable, they do not release cyanide anion readily (i.e. insoluble) and hence nearly nontoxic to the environment [12] as shown in Table 1. Owing to its high affinity for metals, cyanide has been widely employed in extraction and recovery of several value streams (base metals, precious metals and rare earth metals) [13]

Sr #	Cyanide Species	Examples Present in Typical Waste Environment
1	Free Cyanide	CN <sup>-</sup> , HCN
2	Simple Cyanide Compounds	
	a) Readily soluble	NaCN, KCN, Ca(CN) <sub>2</sub> , Hg(CN) <sub>2</sub>
	b) Relatively Insoluble	Zn(CN) <sub>2</sub> , CuCN, Ni(CN) <sub>2</sub> , AgCN
3	Weak Metal – Cyanide Complexes	Zn(CN) <sub>4</sub> <sup>2-</sup> , Cd(CN) <sub>3</sub> <sup>-</sup> , Cd(CN) <sub>4</sub> <sup>2-</sup>
4	Moderately Strong – Cyanide Complexes	Cu(CN) <sub>2</sub> <sup>-</sup> , Cu(CN) <sub>3</sub> <sup>2-</sup> , Ni(CN) <sub>4</sub> <sup>2-</sup> , Ag(CN) <sub>2</sub> <sup>-</sup>
5	Strong Metal – Cyanide Complexes	Fe(CN) <sub>6</sub> <sup>3-</sup> , Fe(CN) <sub>6</sub> <sup>4-</sup> , Co(CN) <sub>6</sub> <sup>4-</sup> , Au(CN) <sub>2</sub> <sup>-</sup> , Hg(CN) <sub>4</sub> <sup>2-</sup>

*Table 1. Relative Stability of Metal Cyanide Compounds & Complexes in Water (Listed in approximate order of increasing stability) [14].*

#### 1.4 WORLDWIDE CYANIDE PRODUCTION

Through the decades many chemicals and lixivants have been studied and investigated for the replacement of cyanide. But still, cyanide holds its position and is given priority over others since it is cost effective, efficient in recovery, and has a widely available number of combinations. Nearly > 90 % of gold and silver extraction around the globe is carried out using cyanide [15]. The worldwide cyanide production goes as high as 1.4 million tons per annum, out of which only a small portion i.e. 13% is used in the production of cyanide reagents for gold and silver mining and recovery, while the rest of 87% is consumed in industrial activities [16].

#### 1.5 CYANIDE GENERATION IN REFINERY

Ammonia, hydrogen cyanide (HCN), and other nitrogen compounds are discharged during the cracking of organic nitrogen compounds in petroleum feedstocks from fluid catalytic cracking unit (FCCU). A principal area of concern related to the hydrocracking and FCC processes is the formation of cyanide as well as its downstream effects.

Gas phase reaction products such as H<sub>2</sub>S, HCN, NH<sub>3</sub>, and hydrocarbons that are formed in the FCC reactor are conveyed to a distillation column. In the distillation column, steam is introduced into the overhead stream for the purpose of reducing the partial vapor pressure of hydrocarbon to allow the operation to be carried out under lower temperatures. The sour water formed in this step combines with HCN and NH<sub>3</sub>. The ammonia cyanide (NH<sub>4</sub>CN) formed by

the reaction of the HCN and NH<sub>3</sub> is ionized in the sour water and discharges ammonium ions (NH<sub>4</sub><sup>+</sup>) and cyanide ions (CN<sup>-</sup>). These cyanide ions escape downstream of the process and is discharged into the environment. This study outlines the treatment of such refinery wastewater having a concentration of 12 ppm free cyanide along with other hydrocarbons, the sample of wastewater received from a confidential petroleum refinery in South Korea is as below;

Compound	Unit	Quantity
COD	mg/L	117
pH (23.3 °C)	--	9.3
Suspended Solids	mg/L	18
Color	Hazen Units	437
CN <sup>-</sup>	mg/L	12.1
Fe	mg/L	1.49
Zn	mg/L	0.02
Mn	mg/L	0.03
Cl <sup>-</sup>	mg/L	128
SO <sub>4</sub> <sup>2-</sup>	mg/L	230
HCHO	mg/L	0.120
Acrylonitrile	mg/L	0.332
Diethylhexyl phthalate	mg/L	0.015
Naphthalene	mg/L	0.230
Benzene	mg/L	4.87
Toluene	mg/L	1.44
Xylene	mg/L	5.57
Phenol	mg/L	0.044
1,2 – dichloroethane	mg/L	0.620
Total N	mg/L	89.4
Total P	mg/L	0.74

*Table 2. Composition of as received refinery wastewater subjected to cyanide removal.*

## 1.6 CYANIDIE RELEASE TO ENVIRONMENT

Cyanide can enter surface water through releases from industries using cyanides and its derivatives (e.g., metal finishing industries, iron and steel mills), runoff from disposal of cyanide wastes in landfills, pesticides and the use of cyanide-containing road salts [17]. Cyanide is usually found at very low concentrations in drinking water sources [18]. Soluble cyanide compounds (e.g. HCN, KCN) are mobile in soils and have low adsorption to soils with high pH, high carbonate and low clay content [19]. Cyanide may leach to groundwater [20]. Under typical conditions in natural waters (pH less than 9.2), most free cyanide is expected to convert

to hydrogen cyanide that is highly volatile [19]. Thus, volatilization from water surfaces is expected to be an important fate process. Cyanide is not likely to accumulate in aquatic life [20]. Cyanide release in different mediums released from anthropogenic sources is shown in Table 3.

Type of sample	Source of sample	Concentration
Atmosphere	Smoking tobacco	0.5 mg/cigarette
	Automobile exhaust:	
	Adverse conditions	Max 10 mg/kg
	Equipped with catalytic convertor	1.1 mg/kg
	Gold field	0.76 ppb
	Fire	1.8±3 µg/m <sup>3</sup>
Water	<b>Electroplating waste:</b>	
	Total cyanide	0.2; max. 3mg/kg
	Dissociable cyanide	0.07 mg/kg
	Complex cyanide	0.2 mg/kg
	Thiocyanate	0.02 mg/kg
	<b>Road salt dock:</b>	
	Total cyanide	25.6 mg/kg
	Dissociable cyanide	2.9 mg/kg
	Complex cyanide	23.1 mg/kg
	Thiocyanate	0
	Gold cyanidation solution	540 mg/kg
	<b>Oil refineries:</b>	
	Total cyanide	0.01; max. 4mg/kg
	Dissociable cyanide	0
Complex cyanide	0.0. Mg/kg	
Thiocyanate	2.2 mg/kg	
Soil	Coking plant sites (France)	46.5±14.5 mg/L
	Gold mine (Brazil)	0.83-1.44 mg/kg
	Techatticup (Mine sites in USA)	<0.01 mg/kg
	Coking plant sites (Germany)	0.14 mg/L

*Table 3. Cyanide concentrations in the atmosphere, water, and soil from anthropogenic sources [8].*

## 1.7 CYANIDE NATIONAL AND INTERANTIONAL STANDARDS AND REGULATONS

Many countries have stringent legislation and severe civil and criminal fine arising from the accidental and international violation of the codes and standards. Nevertheless, there are always risk associated with the use of cyanide, and accidents do happen. Both national and

international regulations and standards regarding free cyanide (i.e. CN<sup>-</sup>), in water environment are summarized in Table 4.

<b>Agency</b>	<b>Description</b>	<b>Standard</b>
<u>NATIONAL</u>		
ME, ROK	Ground water (drinking)	
	• Cyanide	≤ 0.01
	Ground water (non-drinking)	
	• Cyanide (domestic and agricultural water)	≤ 0.01
	• Cyanide (industrial water)	≤ 0.02
<u>INTERNATIONAL</u>		
EPA, US	Cyanide (Drinking Water, MCL)	0.02
WHO, US	Cyanide (Drinking Water)	0.07

*Table 4. National and International regulations applicable to cyanide in drinking water [21], [22], [23].*

## 1.8 HUMAN TOXICITY

Cyanide toxicity levels that can lead to human death are well defined. Intoxication above 2000 ppm hydrogen cyanide can potentially lead to sensation of drying, throat burning, suffusing warmth and need for air. In some cases, cardiovascular failure may also occur, although the heart may continue to beat for 3 to 4 minutes after the last breath. Other signs such as bitter-almond like odor on the breath and rose-colored hue of the skin have also been reported. The total absorbed dose of hydrogen cyanide as low as 0.7mg/kg can even be fatal [15].

Cyanide exerts its primary toxicological effects by binding and inactivating several enzymes, particularly those containing Iron (in ferric state, Fe<sup>3+</sup>) and Cobalt. It is believed that the ultimate lethal effect of anoxia is exerted as cyanide binds itself to the active sites of cytochrome *c* oxidase, the terminal protein in the electron transport chain located within mitochondrial membranes. So, preventing the transfer of electrons to molecular oxygen. Thus, despite of oxygen presence in the blood, it cannot be utilized in Adenosine Triphosphate (ATP) generation, thereby stopping aerobic cell metabolism [2].

## 1.9 CYANIDE ANALYSIS METHODS

A brief comparison of cyanide analysis methods is shown in Table 5. The most widely used and reliable method to analyze free cyanide is by titration with silver nitrate in the presence of potassium iodide or rhodanine as an indicator. However, if metal species exist in solution (other than strong-metal cyanide complexes), the free cyanide concentration is overestimated by this



method. This problem has been observed in industrial plants since it causes a decrease in the leaching efficiency of ore refining process for the same measured ‘free cyanide’ concentration

Analyte	Method	Comments
Free cyanide	AgNO <sub>3</sub> titration	Preferred method For process solutions primarily above 1 mg/L LQL <sup>1</sup> : 1 mg/L HCN (aq), CN <sup>-</sup> , Zn(CN) <sub>x</sub> , parts of Cu(CN) <sub>4</sub>
	AgNO <sub>3</sub> titration with potentiometric end point detection	Alternate method Precise method of end point determination, measures same species as primary method.
	Micro diffusion of HCN from static sample into NaOH [ASTM D4282]	Alternate method Close to ‘free cyanide’
	Ion selective electrode	Alternate method Close to ‘free cyanide’
	Direct colorimetry	Alternate method HCN (aq), CN <sup>-</sup> , Zn(CN) <sub>x</sub> , parts of Cu(CN) <sub>4</sub>
	Amperometric determination	Alternate method Measures same species as primary method
WAD cyanide	Manual distillation pH 4.5 + potentiometric or colorimetric finish [ISO/DIS 670./2, DIN 38405 Part 13.2:1981-02]	Preferred method LQL <sup>1</sup> : 0.05 mg/L HCN (aq), CN <sup>-</sup> , Zn/Cd/Cu/Ni/Ag(CN) Better results than ASTM method in presence of high copper concentrations
	SFIA in line micro-distillation pH 4.5 + colorimetric finish [ASTM D4374]	Alternate method Measures same species as primary method
	FIA in-line ligand exchange + amperometric finish [US-EPA OIA-1677]	Alternate method Measures same species as primary method
	Picric acid, colorimetric determination	Alternate method Measures same species as primary method
Total cyanide	Manual distillation + titration/potentiometric or colorimetric finish [ISO/DIS 6703/1.DIN 38405 Part 13.1:1981-02]	Preferred method LQL <sup>1</sup> : 0.10 mg/L HCN (aq), CN <sup>-</sup> , Zn/Cd/Cu/Ni/Ag/Fe(CN) <sub>x</sub> , parts of Au/Co/Pt/Pd(CN) <sub>x</sub>
	SFIA in line UV irradiation, micro distillation + colorimetric finish [ASTM D4374]	Alternate method Measures same species as primary method also Cr(CN) <sub>x</sub> and better recovery of Au/Co/Pt/Pd(CN) <sub>x</sub>

**Table 5.** Available cyanide analysis technologies based on cyanide classification.

and has been corroborated and reported by several authors. Upon titration, the ionic silver reacts with ionic cyanide to form argento-cyanide ion, as per equation 1



Once all the free cyanide has been consumed by the silver ions, if no indicator is present, the added silver reacts with argentocyanide ion to form white silver cyanide solid AgCN, a yellowish silver iodide (AgI) when potassium iodide is used as an indicator, and a light purple silver rhodanine complex (Ag - Rh), in case of rhodanine as an indicator. The end point is noted at the development of turbidity owing to the formation of silver cyanide or silver iodide, or the shift to light purple hue in the solution. The volume consumed of the silver nitrate can be directly related to free cyanide concentration in the analyzed solution [24].

However, to eliminate the human error in visualizing the endpoint, a spectrophotometric method (for the determination of free and readily liberated cyanide, USEPA approved for wastewater) was adopted to detect the endpoint with respect to change in color intensity which is discussed in later parts of this dissertation.

## **1.10 REMOVAL OF CYANIDE FROM WATER AND WASTEWATER**

Even though, there are many commercially available and scientifically proven technologies for the recovery or destruction of cyanide, but still it is widely discussed and analyzed because of its potential toxicity and environmental impact [25]. However, the prime focus of this study has been on cyanide treatment by nZVI oxidation/corrosion. The objective behind this specific method underlies in the selectivity of cyanide by iron species in a refinery wastewater contaminated with other hydrocarbons and free ions. A brief comparison of proven cyanide remediation or destruction technologies is given Table 3.

Cyanide removing/destroying method	Process mechanisms
Natural Attenuation/Degradation (Collecting and Holding in Ponds)	<ul style="list-style-type: none"> <li>• Volatilization</li> <li>• Biodegradation</li> <li>• Oxidation (by UV, microorganisms)</li> </ul>
Chemical Addition Under Controlled Conditions	
<ul style="list-style-type: none"> <li>• Oxidation Processes <ul style="list-style-type: none"> <li>SO<sub>2</sub>-Air Oxidation Process</li> <li>Alkaline Chlorination <ul style="list-style-type: none"> <li>- Chlorine Gas</li> <li>- Hypochlorites</li> <li>- Electrolytic (in-situ) generation</li> </ul> </li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Oxidation</li> <li>• Conversion to Cyanate</li> <li>• Hydrolysis</li> </ul>
<ul style="list-style-type: none"> <li>Ozonation</li> <li>Sunlight (UV) catalyst</li> <li>Hydrogen Peroxide Oxidation</li> </ul>	<ul style="list-style-type: none"> <li>• Oxidation Complexation</li> <li>• Hydrolysis</li> <li>• Precipitation</li> </ul>
<ul style="list-style-type: none"> <li>• Iron Sulfide Processes</li> <li>• Thermal treatment under high pressure</li> <li>• Fe/Cu precipitation</li> </ul>	
Biological oxidation	
<ul style="list-style-type: none"> <li>• In reactors and under controlled conditions</li> <li>• Passive systems</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation (to CO<sub>2</sub> and NH<sub>3</sub>)</li> <li>• Oxidation to NO<sub>3</sub>; then reduction to N<sub>2</sub></li> <li>• Complexation. Adsorption, precipitation etc.</li> </ul>
Conversion to less toxic forms	
<ul style="list-style-type: none"> <li>• Thiocyanide conversion</li> <li>• Ferrocyanide Conversion</li> </ul>	<ul style="list-style-type: none"> <li>• Complexation</li> </ul>
Cyanide recovery by	
<ul style="list-style-type: none"> <li>• SART, AVR, Cyanisorb</li> </ul>	<ul style="list-style-type: none"> <li>• Acidification</li> <li>• Volatilization and Condensation</li> <li>• Re-neutralization</li> <li>• Complexation</li> </ul>
Adsorption Processes	
<ul style="list-style-type: none"> <li>• Ion exchange (also leads to CN recovery)</li> <li>• Activated carbon</li> <li>• Ion flotation</li> </ul>	
Electrolytic Processes	
<ul style="list-style-type: none"> <li>• Cyanide regeneration</li> <li>• Cyanide destruction</li> </ul>	<ul style="list-style-type: none"> <li>• Decomposition</li> </ul>

**Table 6.** Methods available for removing or destructing cyanide along with their process mechanism involved [6].

## 1.11 CYANDIE WASTEWATER REMEDIATION VIA NANO-ZVI

Nanotechnology has a great potential for providing efficient, cost-effective, and environmentally acceptable solutions to face the increasing requirements on quality and quantity of fresh water for industrial, agricultural, human use and even wastewater treatment. Iron nanomaterials, either zerovalent iron (nZVI) or iron oxides (nFeO<sub>x</sub>), present key physicochemical properties that make them particularly attractive as contaminant removal agents for water and soil cleaning. The large surface area of these nanoparticles imparts high sorption capacity to them, along with the ability to be functionalized for the enhancement of their affinity and selectivity. However, one of the most important properties is the outstanding capacity to act as redox-active materials, transforming the pollutants to less noxious chemical species by either oxidation or reduction, such as reduction of Cr (VI) to Cr (III) and dehalogenation of hydrocarbons. Particularly, nano-zero valent iron (nZVI) due to its high activity towards persistent organic contaminant degradation and heavy metal removal has attracted applications in industrial wastewater treatment as well as in situ soil remediation techniques [26].

In the past decades, Iron based catalysts received a wide attention in Advanced Oxidation Processes (AOPs) for wastewater purification due to its cost effectiveness and environment friendly nature [27], [28]. AOPs have been proven to be promising for degradation of refractory pollutants into smaller molecules owing to their generation of free radicals with high redox potential. Specifically, sulfate radical (SO<sub>4</sub><sup>•-</sup>) and hydroxyl radical (OH<sup>•</sup>) with high redox potential of 2.5e3.1 eV and 2.8 eV generated from Oxone (peroxymonosulfate, PMS) or persulfate (PS) activation [29]. Between the sulfate and hydroxyl radicals, sulfate radical is more promising recently owing to the fact that it possess high redox potential, wide application of pH value range and long lifetime (30 - 40 μs) [30]. Generally, sulfate radical could be generated through energy-based activation (e.g., UV [31], microwave [30], ultrasound [32] or thermal energys [33]) and catalytic activation with transition metals e.g. Co<sub>3</sub>O<sub>4</sub> [34], Fe<sub>3</sub>O<sub>4</sub> [35], ferrite [36], zero valent iron (ZVI) [37].

However, agglomeration of nanoscale ZVI was one of the main defects inhibiting the wide application of ZVI in environment pollution remediation. Although many attentions were paid to synthesis of supported ZVI to avoid agglomeration [38], [39], excess process and chemicals led to the increase in cost and environment burden, further in conflict with cost-effectiveness and green chemistry. Powder ZVI was reported for PMS activation for efficient degradation of p-chloroaniline due to its abundancy and cost effectiveness [40]. But, forming iron oxide or

hydroxide on surface through Fe corrosion reduced the availability of iron for PMS activation in practical application. Acceleration of Fe corrosion and removal of corrosion interface to promote PMS activation were required to address the above issues. Fortunately, ultrasound (US) irradiation could accelerate the corrosion of ZVI besides its wide application in PS/PMS activation [41], [42], [43]. In addition, sono-catalytic reactions were widely applied in degradation of dyes [44], [45]. Thus, ultrasound assisted PS/PMS activation could be promise for degradation of dyes. Interestingly, decolorization rate was significantly enhanced through combination of US irradiation with ZVI catalysis [46], and degradation of 4-CP in US/PMS/nZVI process was reported [47]. Although dissolution of ferrous ions was regarded as the main fact contributing to PMS activation [39], homogeneous PMS activation in the presence of Fe<sup>2+</sup> was not as efficient as that in the presence of nZVI [47].

The objective of this work was to explore the US-assisted nZVI corrosion/oxidation for cyanide wastewater remediation and to further investigate the role of nZVI in PMS activation. In this work, cyanide removal efficiency from a refinery wastewater was investigated by coupling US and ZVI, which was compared to other systems in the absence of US or ZVI. Effect of ZVI dosage, pH value on degradation efficiencies were investigated.

## **1.12 ORGANIZATION OF THE DISSERTATION**

**Chapter 1** provides a general introduction of cyanide in the environment, relevant analysis techniques and treatment technologies, and significance of using nZVI for free cyanide water treatment. It further includes organization of dissertation and research objectives and experimental process.

**Chapter 2** provides methods of the preparation of nZVI and cyanide dummy samples. Furthermore, their characterization and effect of factors were analyzed. Also, it includes theory nZVI redox mechanism and its role in water treatment.

**Chapter 3** presents the results obtained for the removal of cyanide from refinery wastewater. nZVI and other available technologies were compared in parallel to further explore the potential of nZVI in wastewater treatment.

**Chapter 4** summaries the essence of this work.

### 1.13 KNOWLEDGE GAPS AND RESEARCH GOALS

Since, we discussed in the earlier parts of this chapter there can be several ways to remove cyanide from water such as complexation, destruction of cyanide ion, adsorption, etc. However, some treatments lead to ineffective removal or even generation of more harmful gases and requires a great deal of money. Based on literature review, there is a possibility to develop cost effective and high efficiency technique for the cyanide wastewater remediation via nZVI complexation pathway.

The objective of this research is to evaluate the potential of nZVI as a new route for the treatment of free cyanide wastewater. The determined objective is proposed as follows:

- Development of economic nZVI from iron sulfate precursor via ion exchange and precipitation method.
- Characterization studies of nZVI.
- Investigation of the effect of several factors on the adsorption removal efficiency including the effect of nZVI dosage and Oxone dosage, pH, contact time, and initial concentration.
- Determination thermodynamics of the system to express the experimental data of nZVI complexation with cyanide.

## CHAPTER 2

### 2.1 MATERIALS AND METHODS

#### 2.1.1 PREPARATION OF REAGENTS

All the chemicals were of AR grade and were purchased from Daejung Chemicals and Metal Co., Ltd, Republic of Korea, and were used without further refinement, unless otherwise stated. The chemicals acquired were Barbituric Acid, Chloramine T, Iron Sulfate Heptahydrate, Sodium Borohydride, Sulfuric Acid and Sodium Hydroxide. Lab processed distilled water was used in all experiments.

#### 2.2 nZVI SYNTHESIS

There exist several physical and chemical methods for the synthesis of nZVI such as grinding, abrasion, lithography, nucleation from homogeneous solutions or gas, annealing at elevated temperatures and reacting with reducing agents. These synthesis methods are grouped under two broad approaches; the bottom-up and top-down approaches;

The bottom-up approach involves assembling individual atoms and molecules to form nano sized structures. It uses a wide range of reductants to convert dissolved iron in solution to nZVI. The top-down approach on the contrary involves the crushing of bulk particles (microscale or granular) of iron to fine nano-sized particles by mechanical or chemical ways. The choice of synthesis method influences both the size and shape of the nano particles produced.

(a)



(b)

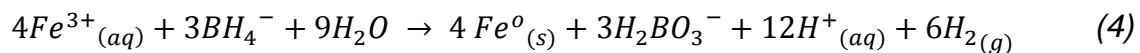
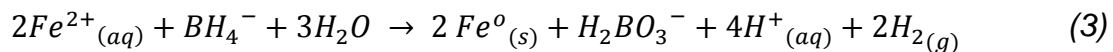
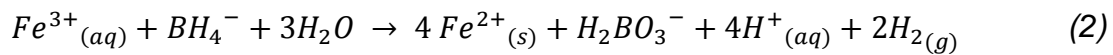


*Figure 3. Magnetic nZVI as synthesized in AEERL via chemical reduction method.*

Among the chemical synthesis methods, the borohydride reduction of ferrous salts is more popularly used due to its simplicity as no special instruments or materials are needed; in

addition, the products have a homogenous structure and are very reactive. Another reason for the preference of this technique is its lower associated cost of production at laboratory scale, estimated to \$200 per kg of nZVI. Most of other techniques for synthesizing nano materials are not feasible or cost-effective for industrial large-scale production. For this reason, the synthesis of nZVI via liquid phase reduction was opted and was achieved by reacting iron salt (ferrous sulfate heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) with a strong reducing agent such as sodium borohydride ( $\text{NaBH}_4$ ) [48]. The chemical reduction method involves following steps:

**(a)** 0.3 M solution of sodium borohydride was prepared in DI water. **(b)** Subsequently, 1 M of ferrous sulfate heptahydrate was prepared in DI water. Then, solution **(a)** was then poured in a burette and added dropwise into the solution **(b)** under sonication and inert atmosphere to avoid oxidation of freshly prepared ZVI. A black precipitate immediately appeared after the first drop of sodium borohydride solution was added. After adding the whole borohydride solution, the mixture was left for further 5 mins under sonication. The redox reaction can be represented by;



Iron nanoparticles were then separated from the liquid phase by filtration, in which two sheets of Whatman filter papers of 0.45  $\mu\text{m}$  were used in each filtration process. At this point, the solid particles were washed three times with portions of absolute ethanol to remove any water. This washing process is probably the key step of synthesis since it prevents the rapid oxidation of zero-valent iron nanoparticles. The synthesized nanoparticles were finally dried in oven at 105°C till overnight.

### 2.3 CHARACTERIZATION

The nanostructures of ZVI and iron cyano complex were investigated through the wide-angle X-ray Diffraction (XRD) patterns, performed on a Bruker D8 Advance X-ray diffractometer equipped with nickel-filtered  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), at scanning angle ( $2\theta$ ) maintained between 10–80° at a scanning rate of 2°  $\text{min}^{-1}$ , having a voltage of 40 kV and 40 mA current intensity. The peak at  $2\theta$  of 44.736° indicates the existence of iron nanoparticles ( $\text{Fe}^0$ ). Particle size can be presumed with the XRD by using Scherer equation [49]:

$$D = 0.9 \lambda / \beta \cos \theta \quad (5)$$



where  $D$  is the size of particle (nm),  $\beta$  is the full width at half maximum (FWHM),  $\lambda$  is the Cu  $K\alpha$  radiation wavelength, and  $\theta$  is the Bragg angle obtained from  $2\theta$  corresponding to maximum peak intensity [50].

The surface electronic states and chemical compositions were revealed by X-ray Photoelectron Spectroscopy (XPS) analysis (Thermo Fischer Scientific - ESCALABMK 250 XI system) by using Al  $K\alpha$  Xray ( $h\nu = 1486.6$  eV) anode. The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface areas (SA) of as-prepared catalysts by the adsorption-desorption of nitrogen at 77 K (Micromeritics Instruments ASAP 2020). The morphology and nanostructure were studied by Field Emission - Scanning electron micrographs (FE - SEM) by employing FEI Nova NanoSEM.

## **2.4 EXPERIMENTATION**

The wastewater as received from refinery was of primary interest for cyanide reduction. The sample was first subjected to paper filtration using Whatman qualitative filter paper grade 100 to remove any carbon residue suspended or otherwise settled down within the sample. The filtered samples (20 ml each) were then subsequently treated with different catalyst loading of nZVI under sonication conditions. The treated sample was matured for 15 min and then again subjected to paper filtration, in order to collect the iron-cyano complex and unreacted nZVI, these precipitates were kept in a muffle furnace overnight to achieve high crystallinity for XRD analysis and to remove the moisture.

For the determination of free and readily liberated cyanide a USEPA approved spectrophotometric method was taken into consideration. The method corresponds to DIN 38405-13 and is analogous to ISO 6703, EPA 335.2, APHA 4500-CN- E, and ASTM D2036-09 D. Having a measuring range of 0.010 – 0.500 mg/l  $CN^-$ . Cyanide ions react with a chlorinating agent (chloramine – T) to form cyanogen chloride, which in turn reacts with 1,3-dimethylbarbituric acid to form a violet dye (pyridine-free König reaction). This dye is then determined photometrically. This method, however, measures free cyanide only, in order to measure readily liberated cyanide samples must be subjected to digestion.

## **2.5 THERMODYNAMICS**

The reactions taking place during cyanide complexation are presented in Table, along with their reaction standard Gibbs free energy at 25°C.

For a solution containing 12 ppm Free Cyanide at 1 atm and 25°C, the change in Gibbs free energy of these reactions can be computed using equations (2) and (3)

$$aV + bX = cY + dZ \quad (6)$$

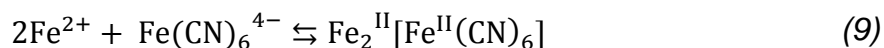
Where, lowercase letters represent the number of moles of the species involved in the reaction, capital letters stand for the species and braces for the activity (activity co-efficient multiplied by species concentration)

The activity co-efficient of aqueous species were considered as equal to 1, as the concentration of species in solution is below  $1 \times 10^{-3}M$ .

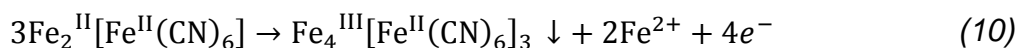
$$\Delta G = \Delta G^o + RT \ln K \quad (7)$$

Here,  $K$  is the equilibrium constant, function of the temperature and molecular orientation/geometry.

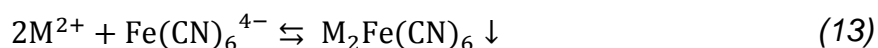
As soon as the catalyst is added to the sample, the reactions would take place following a sequence from more negative to less negative change in Gibbs free energy, as indicated in Table 4. Since there are no ferric species as the reaction is commenced, the only available ferrous ion produced by nZVI corrosion under sonication would react with free cyanide to form ferrocyanide complex (equation 5), which makes it the first step of the reaction mechanism. Once all the free cyanide has been consumed to form ferrocyanide complex, the surplus ferrous ions immobilize it and yields a stable insoluble complex,  $Fe_2[Fe(CN)_6]$ , as shown in the reactions below:



The insoluble white ferrous ferrocyanide product rapidly absorbs oxygen from the air and turns deep blue (black to the naked eye), with the formation of ferric ferrocyanide. The following redox couple could account for the reaction:



In addition to this, cyanide would also amalgamate with any known metal specie present in the solution or added afterwards to form mixed metal cyanide. A general reaction depicting cyanide combination with other metal specie/s is shows as;



Complexation Reaction/s	Std. Gibbs free energy	Equation
	$\Delta G^{\circ}$ (kcal)	
$Fe^{3+} + 6CN^{-} \rightleftharpoons Fe(CN)_6^{3-}$	-68.62	(14)
$Fe^{2+} + 6CN^{-} \rightleftharpoons Fe(CN)_6^{4-}$	-59.14	(15)
$Fe^{3+} + 3OH^{-} \rightleftharpoons Fe(OH)_3 (s)$	-51.76	(16)
$Fe^{3+} + 2OH^{-} \rightleftharpoons Fe(OH)_2^{+}$	-28.79	(17)
$Fe^{2+} + 2OH^{-} \rightleftharpoons Fe(OH)_2 (s)$	-20.52	(18)
$Fe(CN)_6^{4-} + 6H^{+} \rightleftharpoons Fe^{2+} + 6HCN$	-16.345	(19)
$H^{+} + CN^{-} \rightleftharpoons HCN$	-12.58	(20)
$Fe(CN)_6^{4-} + 2H^{+} \rightleftharpoons H_2Fe(CN)_6^{2-}$	-8.77	(21)
$Fe^{2+} + OH^{-} \rightleftharpoons FeOH^{+}$	-6.38	(22)
$Fe(CN)_6^{4-} + H^{+} \rightleftharpoons HFe(CN)_6^{3-}$	-5.77	(23)

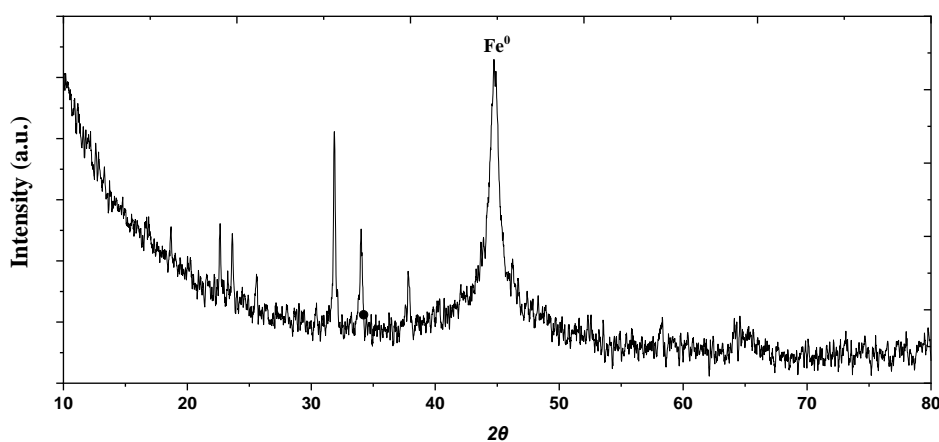
**Table 7.** Standard Gibbs Free Energy of complexation reactions at 25°C (HSC Chemistry database v6.00).

## CHAPTER 3

### 3.1 RESULTS AND DISCUSSION

#### 3.1.1 XRD ANALYSIS

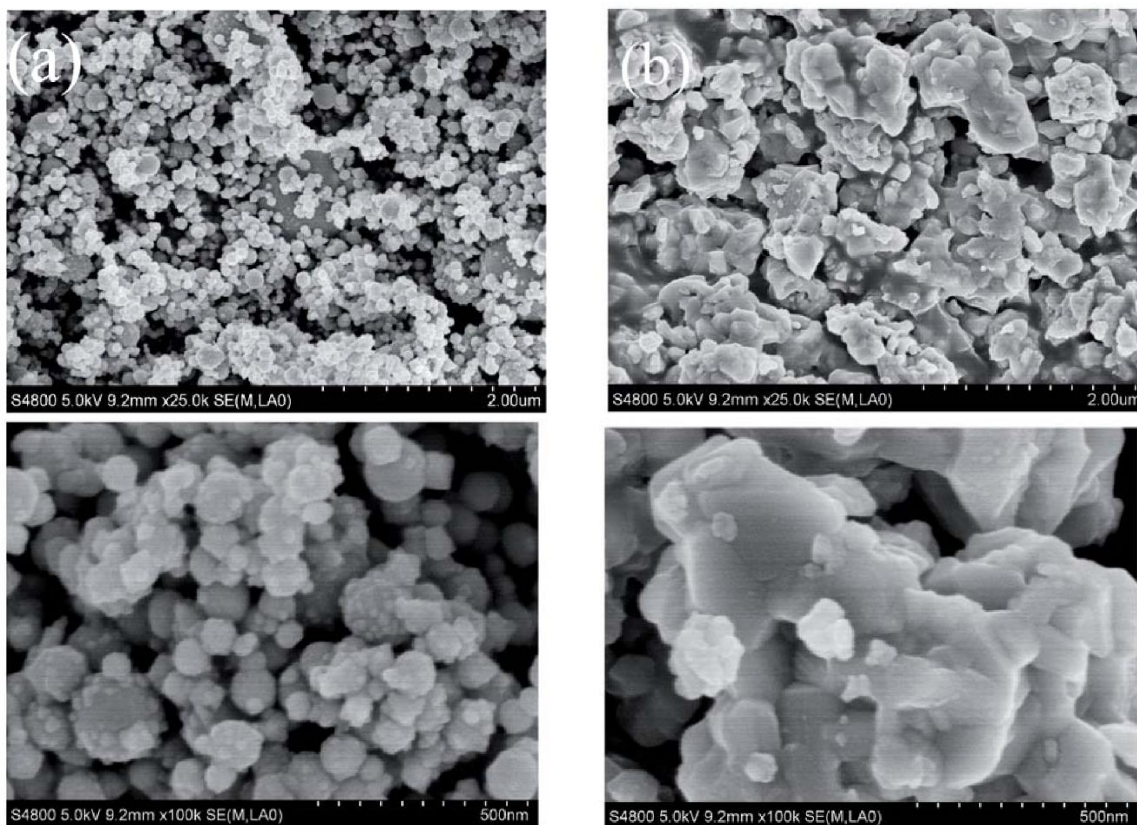
Figure 4. shows the XRD analysis of  $\text{Fe}^0$  nanoparticles. The peak at  $2\theta$  of  $44.736^\circ$  which represent high intensity indicates the presence of  $\alpha\text{-Fe}0$  nanoparticles in the sample. The peak at  $2\theta = 31.857^\circ$  indicate the existence of iron oxide ( $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ). The mean crystalline dimension of the  $\text{Fe}^0$  nanoparticle was found to be 44.43 nm and lattice strain to be 0.0021 when calculated by Scherer equation. Similar results were observed in other studies [53], [54].



*Figure 4. X-ray Diffraction (XRD) pattern of nZVI particles.*

#### 3.1.2 SEM ANALYSIS

Figure 5. (a) shows the SEM images of the synthesized nZVI. The iron particles appear spherical and demonstrates the characteristic of chain-like morphology. While on the other hand in Figure 5. (b), nZVI synthesis in the absence of sonication led to the formation of relatively larger particles, aggregation of which is reported to be caused by the magnetic dipole–dipole interactions and large surface area. Similar results were observed in other studies [53], [55]. Literature resources indicate that nZVI possess a core–shell structure, in which the shell represents the oxidized part that surrounds the Fe core and preserves it against further oxidation.

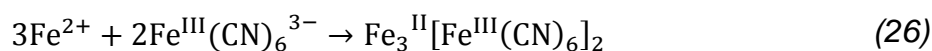
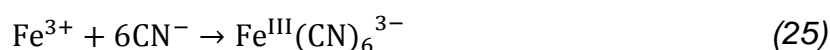


**Figure 5.** Scanning electron microscopy of nZVI (a) prepared under sonication (b) prepared without assistance of sonication.

### 3.1.3 EFFECT OF IRON TO FREE CYANIDE RATIO

The stoichiometry of reactions from (5) to (8) demands a Fe:CN<sup>-</sup> molar ratio of 0.39. The effect of variations in Fe:CN<sup>-</sup> ratio on the resultant solution is shown in Figure 1. Theoretically, complete conversion to Fe(CN)<sup>6-</sup> is achieved at a molar ratio of 0.17.

It is imperative to mention that the pH value of the sample solution varied between 4.5 to 8.0 depending on the nZVI concentration, this could be explained as a result of hydrolysis of Fe<sup>+2</sup> ions in the aqueous solution. The decrease in pH after the two solutions have been mixed is probably due to the slow oxidation of Fe(II) to hydrated Fe(III) oxides, a process that involves further hydrolysis and the liberation of protons. At Fe:CN<sup>-</sup> ratio of 0.5 and higher, only after a few minutes after the reaction, a concentration of 1.5 ppm of free cyanide was detected. The cyanide level may be reduced to below the detection limit (0.02 mg/l) by an increase in either the reaction time or Fe:CN<sup>-</sup> ratio. Following reactions may occur to some extent:



Many authors and scientist have suggested a higher molar ratio for the effective removal of cyanide, to keep the complexation equilibrium reaction in the forward direction. But this would be an unnecessary excess, resulting in high reagent consumption and making it economically unviable. A successful 98% removal of cyanide is achieved with an optimum nZVI loading of 0.0075 mg as show in table below. Such a low amount of catalyst can be explained by low content of free cyanide present in the wastewater, even though this catalyst loading is still however 3 times higher as compared to cyanide content i.e. 12 ppm.

<b>KCN Solution (11.5 ppm)</b>	<b>Catalyst loading (n-ZVI, µg)</b>	<b>Total Cyanide Detected after treatment (ppm)</b>	<b>Percentage Removal Efficiency</b>
A	1.0	5.4	53 %
B	2.5	2.9	74 %
C	5.0	1.1	90 %
D	7.5	0.3	98 %

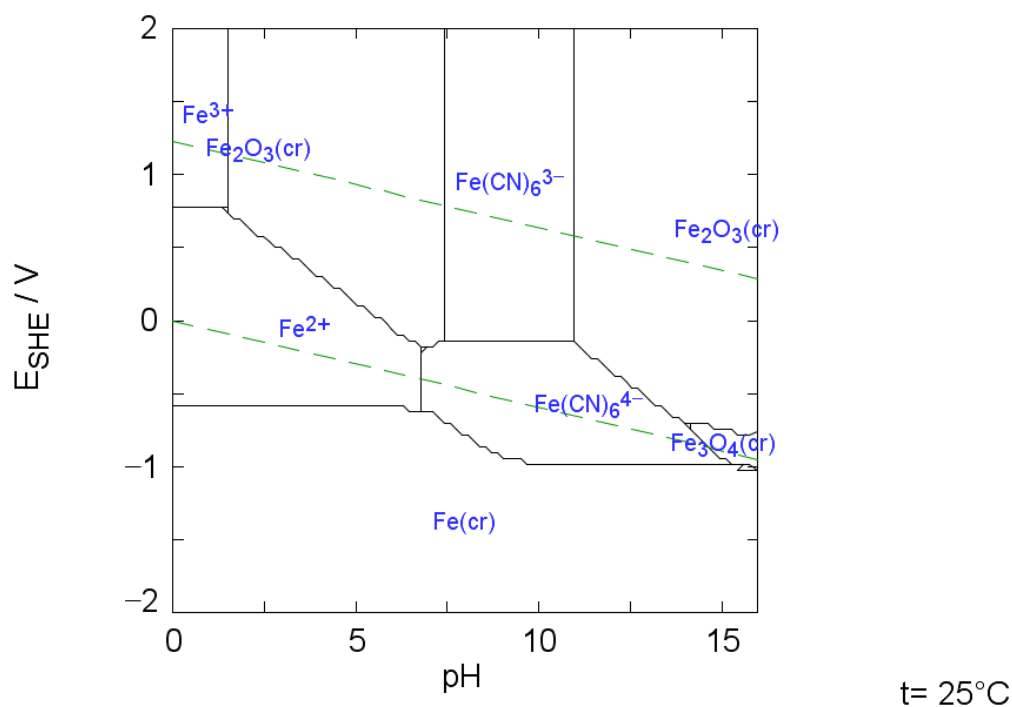
*Table 8. Effect of nZVI catalyst loading for the removal of cyanide from wastewater.*

### 3.1.4 STABILITY OF COMPLEXES

To depict the stability region of the iron-cyano complexes Pourbaix diagram has been taken into account, the diagram is constructed by computing the equilibrium between two adjacent species from their activities, obtained by means of Spana computer program, exclusively based on HALTAFALL algorithm. For Fe-CN-H<sub>2</sub>O system using (Fe:CN<sup>-</sup> = 0.1 or) [Fe<sup>+2</sup>] = 0.0000462 and [CN<sup>-</sup>] = 0.000462 mol/L (12 ppm cyanide) the area of predominance for the various iron species and iron-cyanide complexes is shown in Figure 6. Such a low concentration enables us to safely assume the activity coefficient to be unity and impedes precipitation of the solid phases which hide the area of dominant aqueous species in the Eh-pH diagram.

$$[\text{Fe}^{2+}]_{\text{TOT}} = 46.20 \mu\text{M}$$

$$[\text{CN}^-]_{\text{TOT}} = 0.46 \text{ mM}$$



**Figure 6.** Eh-pH diagram for the Fe-CN-H<sub>2</sub>O system at 25°C. Free energy data for Fe<sup>+2</sup> and CN<sup>-2</sup> extracted from Spana Hydrochemical logK Database (cross checked with HSC Chemistry v6.00 and Visual MINTEQ).

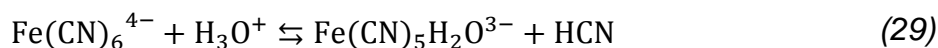
It is evident from the above diagram, the Fe(CN)<sub>6</sub><sup>4-</sup> species are thermodynamically unstable with respect to oxidation within the region of stability of water, as shown by bounded broken lines, the ion is also clearly unstable with respect to changes in pH. Table 5. Represents the solubility product of iron cyanide complexes, the reactions mentioned in table are written with products as completely dissociated species for consistency. However, the metal-metal complex cyanide solids usually do not dissociate completely to produce free cyanide under environmental conditions.

Solid and Dissolution Reaction	Solubility Product [51] (log <i>k</i> <sub>sp</sub> at 25°C, I=0)	Eq.
$\text{Fe}_4^{\text{III}}[\text{Fe}(\text{CN})_6]_3 = 4\text{Fe}^{3+} + 3\text{Fe}^{2+} + 18\text{CN}^-$	-263.60	(27)
$\text{Fe}_3^{\text{III}}[\text{Fe}(\text{CN})_6]_2 = 3\text{Fe}^{3+} + 2\text{Fe}^{2+} + 12\text{CN}^-$	-177.40	(28)

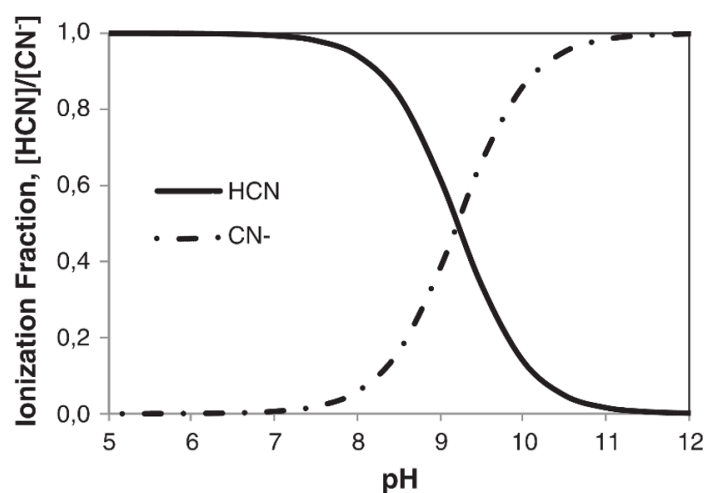
### 3.1.5 EFFECT OF pH

An optimum pH is very crucial for complexation of iron and cyanide, a lower pH value result in incomplete precipitation and would cause acid attack/protonation to ferrous cyanide complex as illustrated in Equation (28) and (29), whereas a higher pH would result in decomposition of

the product. Thus, a mid-range pH is essential, an optimum equilibrium pH range for the precipitation of Prussian blue is between 5.5 and 6.5 and under these conditions it is possible to achieve very low levels of cyanide species in the test sample [52]. In the present work, the pH of the solution was adjusted in between 4.5-7 of reaction solution when the it encounters cyanide solution (having a natural pH value of 8.87).



The presence of  $\text{CN}^-$  and  $\text{HCN}$  as the function of pH is presented in figure 7. According to this figure, under alkaline conditions ( $\text{pH} > 10.5$ ), the dominant species are  $\text{CN}^-$ . At the lower pH values (around 9.3), there is the equivalent concentration of  $\text{CN}^-$  and  $\text{HCN}$ . In addition, free cyanide is present as  $\text{HCN}$  from the neutral to acidic conditions ( $7.0 < \text{pH} < 8.3$ ).



**Figure 7.** HCN and cyanide anion concentration fraction as a function of pH in aqueous solutions at 25 °C.



## CHAPTER 4

### 4.1 CONCLUSION

In short, a new pathway for cyanide removal has been put forth. nZVI was successfully synthesized by a facile chemical reduction method and was applied to cyanide complexation. The catalyst was comprehensively characterized through different techniques including XRD, SEM-EDS, XPS. The current study revealed effective results and high efficiency as compared to other complexation routes, such as complexation with iron sulfate solution. The nZVI hold an advantage and possess an ability to act as a redox active material as compared to other metal complexation routes. The nZVI synthesized under sonication conditions tend to form regular spherical like structures, while the absence of sonication during the nZVI synthesis lead to the formation of relatively large particles possessing an irregular shape. Furthermore, owing to its cost effectiveness and relative abundance, it could be proved a promising pathway for cyanide removal from water either polluted or clean. The best results have been obtained at a nZVI catalyst loading of 0.3 mg/l and slightly lower pH (5.5 to 6.5). A cyanide removal efficiency of 99% from refinery tailings has been successfully achieved.

## REFERENCES

- [1] G. Mapstone, B.J.J.O.A.C. Thorn, BIOTECHNOLOGY, Hypochlorite oxidation of cyanide and cyanate, 28 (1978) 135-143.
- [2] S.I. Baskin, J.B. Kelly, B.I. Maliner, G.A. Rockwood, C. Zoltani, Cyanide poisoning, Medical aspects of chemical warfare, 11 (2008) 372-410.
- [3] A. Akcil, C. Erust, C.S. Gahan, M. Ozgun, M. Sahin, A.J.W.M. Tuncuk, Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixivants—a review, 45 (2015) 258-271.
- [4] A.J.M.P. Akcil, E.M. Review, A New Global Approach of Cyanide Management: International Cyanide Management Code for the Manufacture, Transport, and Use of Cyanide in the Production of Gold, 31 (2010) 135-149.
- [5] R. Gracia, G. Shepherd, Cyanide poisoning and its treatment, Pharmacotherapy: The Journal of Human Pharmacology and Drug Therapy, 24 (2004) 1358-1365.
- [6] N. Kuyucak, A. Akcil, Cyanide and removal options from effluents in gold mining and metallurgical processes, Minerals Engineering, 50 (2013) 13-29.
- [7] F.P. Simeonova, L. Fishbein, W.H. Organization, Hydrogen cyanide and cyanides: human health aspects, (2004).
- [8] A. Mousavi, Analysis of cyanide in mining waters, (2018).
- [9] P.J. Fischer, D.A. Tarr, Gary L. Miessler.
- [10] T.I. Mudder, M. Botz, A. Smith, Chemistry and treatment of cyanidation wastes, Mining Journal Books, London, UK, (2001).
- [11] D.A. Dzombak, R.S. Ghosh, G.M. Wong-Chong, Cyanide in water and soil: chemistry, risk, and management, CRC press 2005.
- [12] C. Harper, N. Roney, J. Taylor, Toxicological profile for cyanide, (2006).
- [13] T. Lister, L. Diaz, G. Clark, P. Keller, Process Development for the Recovery of Critical Materials from Electronic Waste, Idaho National Lab.(INL), Idaho Falls, ID (United States), 2016.
- [14] A. Smith, D.W. Struhsacker, Cyanide geochemistry and detoxification regulations, Introduction to Evaluation, Design and Operation of Precious Metal Heap Leach Projects, SME, Littleton, Colorado, (1988) 275-305.
- [15] T. Mudder, M.J.E.J.o.M.P. Botz, E. Protection, Cyanide and society: a critical review, 4 (2004).

- [16] M.J. Logsdon, K. Hagelstein, T. Mudder, The management of cyanide in gold extraction, International Council on Metals and the Environment Ottawa 1999.
- [17] B.o.R. U.S. Department of the Interior, Cyanide Fact Sheet, 2001.
- [18] WHO, Cyanide in drinking water: Background document for development of WHO guidelines for drinking water quality (WHO/SDE/WSH/03.04/05), World Health Organization Geneva, 2007.
- [19] USEPA, Technical Factsheet on: Cyanide, (2009).
- [20] [http://www.epa.gov/OGWDW/contaminants/dw\\_contamfs/cyanide.html](http://www.epa.gov/OGWDW/contaminants/dw_contamfs/cyanide.html), Consumer Factsheet on: Cyanide (2009).
- [21] R.o.K. Ministry of Environment, ECOREA, Environmental Review 2013, (2013).
- [22] O. Water, Edition of the drinking water standards and health advisories, United States, (2012).
- [23] O.m.d.l. santé, W.H. Organization, W.-.-W. programme, W.H.O. Staff, Ś.O. Zdrowia, WHO, Guidelines for drinking-water quality, World Health Organization 2004.
- [24] C. Jimenez-Velasco, F. Nava-Alonso, A. Uribe-Salas, O. Alonso-Gonzalez, Thermodynamic analysis of free cyanide determination by silver nitrate titration in copper bearing solutions, Canadian Metallurgical Quarterly, 53 (2014) 207-212.
- [25] A.J.B.A. Akcil, Destruction of cyanide in gold mill effluents: biological versus chemical treatments, 21 (2003) 501-511.
- [26] N. Aich, C. Su, I. Kim, A. Masud, Application of Nanozerovalent Iron for Water Treatment and Soil Remediation: Emerging Nanohybrid Approach and Environmental Implications, Iron Nanomaterials for Water and Soil Treatment, Jenny Stanford Publishing 2018, pp. 65-87.
- [27] S.O. Ganiyu, M. Zhou, C.A. Martínez-Huitle, Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment, Applied Catalysis B: Environmental, 235 (2018) 103-129.
- [28] P. Nidheesh, Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review, Rsc Advances, 5 (2015) 40552-40577.
- [29] Y. Pang, Y. Ruan, Y. Feng, Z. Diao, K. Shih, D. Chen, L. Kong, Ultrasound assisted zero valent iron corrosion for peroxy monosulfate activation for Rhodamine-B degradation, Chemosphere, 228 (2019) 412-417.
- [30] L. Duan, X. Zhou, S. Liu, P. Shi, W. Yao, 3D-hierarchically structured Co<sub>3</sub>O<sub>4</sub>/graphene hydrogel for catalytic oxidation of Orange II solutions by activation of peroxy monosulfate, Journal of the Taiwan Institute of Chemical Engineers, 76 (2017) 101-108.

- [31] J. Sharma, I. Mishra, D.D. Dionysiou, V. Kumar, Oxidative removal of Bisphenol A by UV-C/peroxymonosulfate (PMS): kinetics, influence of co-existing chemicals and degradation pathway, *Chemical Engineering Journal*, 276 (2015) 193-204.
- [32] C. Cai, H. Zhang, X. Zhong, L. Hou, Ultrasound enhanced heterogeneous activation of peroxymonosulfate by a bimetallic Fe–Co/SBA-15 catalyst for the degradation of Orange II in water, *Journal of hazardous materials*, 283 (2015) 70-79.
- [33] M. Nie, Y. Yang, Z. Zhang, C. Yan, X. Wang, H. Li, W. Dong, Degradation of chloramphenicol by thermally activated persulfate in aqueous solution, *Chemical Engineering Journal*, 246 (2014) 373-382.
- [34] R. Yuan, L. Hu, P. Yu, H. Wang, Z. Wang, J. Fang, Nanostructured Co<sub>3</sub>O<sub>4</sub> grown on nickel foam: an efficient and readily recyclable 3D catalyst for heterogeneous peroxymonosulfate activation, *Chemosphere*, 198 (2018) 204-215.
- [35] C. Tan, N. Gao, Y. Deng, J. Deng, S. Zhou, J. Li, X. Xin, Radical induced degradation of acetaminophen with Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles as heterogeneous activator of peroxymonosulfate, *Journal of hazardous materials*, 276 (2014) 452-460.
- [36] Y. Ren, L. Lin, J. Ma, J. Yang, J. Feng, Z. Fan, Sulfate radicals induced from peroxymonosulfate by magnetic ferrosphenel MFe<sub>2</sub>O<sub>4</sub> (M= Co, Cu, Mn, and Zn) as heterogeneous catalysts in the water, *Applied Catalysis B: Environmental*, 165 (2015) 572-578.
- [37] T. Chung, T. Anh, D. Phung, T. Luong, Degradation of Nitrobenzene by Persulfate Activated with Zero-valent Iron, *Asian Journal of Chemistry*, 24 (2012).
- [38] M.A. Al-Shamsi, N.R. Thomson, S.P. Forsey, Iron based bimetallic nanoparticles to activate peroxygens, *Chemical engineering journal*, 232 (2013) 555-563.
- [39] C. Tan, Y. Dong, L. Shi, Q. Chen, S. Yang, X. Liu, J. Ling, X. He, D. Fu, Degradation of Orange II in ferrous activated peroxymonosulfate system: efficiency, situ EPR spin trapping and degradation pathway study, *Journal of the Taiwan Institute of Chemical Engineers*, 83 (2018) 74-81.
- [40] I. Hussain, Y. Zhang, S. Huang, X. Du, Degradation of p-chloroaniline by persulfate activated with zero-valent iron, *Chemical engineering journal*, 203 (2012) 269-276.
- [41] T. Zhou, T.-T. Lim, Y. Li, X. Lu, F.-S. Wong, The role and fate of EDTA in ultrasound-enhanced zero-valent iron/air system, *Chemosphere*, 78 (2010) 576-582.
- [42] B. Lai, Z. Chen, Y. Zhou, P. Yang, J. Wang, Z. Chen, Removal of high concentration p-nitrophenol in aqueous solution by zero valent iron with ultrasonic irradiation (US–ZVI), *Journal of hazardous materials*, 250 (2013) 220-228.

- [43] J. Cao, L. Lai, B. Lai, G. Yao, X. Chen, L. Song, Degradation of tetracycline by peroxymonosulfate activated with zero-valent iron: performance, intermediates, toxicity and mechanism, *Chemical Engineering Journal*, 364 (2019) 45-56.
- [44] A. Hassani, G. Çelikdağ, P. Eghbali, M. Sevim, S. Karaca, Ö. Metin, Heterogeneous sono-Fenton-like process using magnetic cobalt ferrite-reduced graphene oxide (CoFe<sub>2</sub>O<sub>4</sub>-rGO) nanocomposite for the removal of organic dyes from aqueous solution, *Ultrasonics sonochemistry*, 40 (2018) 841-852.
- [45] R. Mahdavi, S.S.A. Talesh, Enhancement of ultrasound-assisted degradation of Eosin B in the presence of nanoparticles of ZnO as sonocatalyst, *Ultrasonics sonochemistry*, 51 (2019) 230-240.
- [46] X. Wang, L. Wang, J. Li, J. Qiu, C. Cai, H. Zhang, Degradation of Acid Orange 7 by persulfate activated with zero valent iron in the presence of ultrasonic irradiation, *Separation and Purification Technology*, 122 (2014) 41-46.
- [47] G. Barzegar, S. Jorfi, V. Zarezade, M. Khatebasreh, F. Mehdipour, F. Ghanbari, 4-Chlorophenol degradation using ultrasound/peroxymonosulfate/nanoscale zero valent iron: reusability, identification of degradation intermediates and potential application for real wastewater, *Chemosphere*, 201 (2018) 370-379.
- [48] J. Adusei-Gyamfi, V. Acha, Carriers for nano zerovalent iron (nZVI): synthesis, application and efficiency, *RSC advances*, 6 (2016) 91025-91044.
- [49] M. Fan, P. Yuan, T. Chen, H. He, A. Yuan, K. Chen, J. Zhu, D. Liu, Synthesis, characterization and size control of zerovalent iron nanoparticles anchored on montmorillonite, *Chinese science bulletin*, 55 (2010) 1092-1099.
- [50] S. Dutta, A. Ghosh, S. Satpathi, R. Saha, Modified synthesis of nanoscale zero-valent iron and its ultrasound-assisted reactivity study on a reactive dye and textile industry effluents, *Desalination and Water Treatment*, 57 (2016) 19321-19332.
- [51] W.M. Haynes, *CRC handbook of chemistry and physics*, CRC press 2014.
- [52] M. Adams, The removal of cyanide from aqueous solution by the use of ferrous sulphate, *Journal of the Southern African Institute of Mining and Metallurgy*, 92 (1992) 17-25.
- [53] M.R. Taha, A. Ibrahim, Characterization of nano zero-valent iron (nZVI) and its application in sono-Fenton process to remove COD in palm oil mill effluent, *Journal of Environmental Chemical Engineering*, 2 (2014) 1-8.

[54] J. Fan, Y. Guo, J. Wang, M. Fan, Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles, *Journal of Hazardous Materials*, 166 (2009) 904-910.

[55] Ç. Üzüm, T. Shahwan, A.E. Eroğlu, I. Lieberwirth, T.B. Scott, K.R. Hallam, Application of zero-valent iron nanoparticles for the removal of aqueous  $\text{Co}^{2+}$  ions under various experimental conditions, *Chemical Engineering Journal*, 144 (2008) 213-220.