A Study on Removal of Cyanide from Wastewater Using Ion Exchange

By

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Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

(Associate Professor Ir Abdul Aziz Omar)
Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

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CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted for this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been taken or done by unspecified sources or persons.

MOHD YUSSOF BIN YAACOB

EXECUTIVE SUMMARY

Final Year Research Project dissertation is written after the project works has been completed. The dissertation contains the study on Removal of Cyanide from Wastewater Using Ion Exchange which as a requirement to fulfill for Bachelor of Engineering (Hons) (Chemical Engineering). The dissertation comprises of five main chapters which are project background, literature review, methodology and project work, results and discussion plus the conclusion. The first chapter mainly about stress on the project objectives, problem statement and the scope of the study while in chapter two the detail research and literature review is properly done with regards to the objectives and scope of study that has been addressed earlier in chapter one. Chapter three of the dissertation shall discuss on the procedures, laboratory works and methodology used in order to solve the problem statement of the project. The heart of the dissertation is recorded in chapter four. In this chapter, the outcome and results gain from the methodology and project works is analyzed and discussed in great detail. The chapter also delved on the effectiveness of the works that has been conducted through out the time frame given. Last but not least the dissertation is then concluded in chapter five with the justification from those four previous chapters. Overall, the study on Removal of Cyanide from Wastewater Using Ion Exchange is observed to be effective as the method capable of reducing the Cyanide content in wastewater after been treated through the ion exchange unit. According to the quantitative method using HACH Spectrophotometer DR/2010 Cyanide content reduce from maximum 1500 mg/L to as low as 2.17 mg/L. However the effectiveness of ion exchange method in cyanide removal depends on five parameters manipulated in this study which are cyanide concentration, test water flowrate, resin bed height, additional of water hardness ($CaCO_3$) and suspended and colloidal impurities in test water.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Sewage is the wastewater released by residences, businesses and industries in a community. It contains 99.94 percent water, with only 0.06 percent of the wastewater dissolved and suspended solid material. Biochemical Oxygen Demand (BOD_5) is used as a standard for the strength measurement of the wastewater. The BOD_5 concerns on the amount of oxygen required by microorganisms in five days for breaking down sewage process. Untreated sewage has a BOD_5 ranging from 100 mg/l to 300 mg/l. The untreated sewage would bring disease such as skin disease to humans and animal due to Pathogens or disease-causing organisms are present in sewage. Besides micro organisms and suspended solid; sewage also contains nutrients (such as ammonia, phosphorus and cyanide), minerals, and metals. Sewage treatment which involving multi-stage process for wastewater recovery before it re-enters a body of water, land application or been reused. The goal is to reduce or remove all of those unneeded substances as mentioned above and other pollutants from wastewater. Each receiving body of water has limits to the amount of pollutants it can receive without degradation. Thus, each sewage treatment plant must hold a permit listing the allowable levels of BOD_5, suspended solids, coliform bacteria and other pollutants. The National Pollutant Discharge Elimination or NPDES permits is a standard indicator for the discharge permits [2]. This study shall focus on Cyanide removal from wastewater by using ion exchange method, as one of the sewage treatment process. It involves the experimental studies using the ion exchange unit available in the environmental laboratory. The study also required the candidate to make comparison between the findings on Cyanide contamination in Malaysian wastewater and with what was in the World Health Organization (WHO) requirements. The experiment should be conducted by using self-prepared artificial contaminated wastewater or any other equivalent sources and run through the ion exchange unit with several different resins available in the laboratory for efficiency observation purposes.

1.2 Problem Statement

Study on Cyanide level either in Malaysian wastewater or any equivalent data obtained is required as a reference for wastewater treatment process. Further, Cyanide has been reported to be a good marker for substances contained in industries such as organic chemical processing and petroleum industries. Cyanide is a substance that is found in combination with other chemicals in the environment. Of these combinations (compounds), the ones people are most likely to come in contact with are hydrogen cyanide, sodium cyanide, and potassium cyanide. Hydrogen cyanide is a colorless gas or liquid with a faint, bitter almond odor. Sodium cyanide and potassium cyanide are both colorless solids that have a slight odor of bitter almonds in damp air. Cyanides are both man-made and naturally occurring substances. They are found in a number of foods and plants and are produced by certain bacteria, fungi, and algae. The Environmental Protection Agency (EPA) allows levels of cyanide in food ranging from 25 ppm in dried beans, peas, and nuts to 250 ppm in spices. Cyanide levels in the workplace are regulated by the Occupational Safety and Health Administration (OSHA). OSHA has a legally enforceable exposure limit of 5 milligrams of cyanide per cubic centimeter of air (mg/cm3) for cyanide and 11 mg/cm3 (or 10 ppm) hydrogen cyanide in air for an 8-hour workday, 40-hour workweek. Therefore, there is little or no removal of cyanide during sewage treatment processes [1]. There are several separation methods to removed Cyanide from wastewater such as anodic oxidation, chromatography and ion exchange. But in this study, the author shall only focus on the effectiveness of ion exchange method for cyanide removal from wastewater. In general, there are no specific resins that work as a cyanide selective in its function. Therefore, this study also required for the determination of the most appropriate resin type applicable in service especially industries.

1.3 Objectives and Scope of Study

The objectives of this study mainly focus on determining the level of Cyanide in Malaysian wastewater. The cyanide level would be taken from the appropriate literature review or articles if the data was failed to be found in Malaysian wastewater for the purpose of the experiment. The project also studies on the effectiveness of the ion exchange unit in cyanide removal as well as the appropriate resin in services for the process.

The scope of study delved within the self preparation of an artificial waste water, the effectiveness of the ion exchange lab scale unit (SOLTEQ) in cyanide removal and the analysis of the cyanide content of the test water sample after run through the ion exchange unit. The resin type used also limited to the resin available on site. The time frame allocated with only 14 weeks for study completion, the only manageable scope of study just as mentioned above. Improvement and more detail with regards to the study could be conducted if the time allocation is longer.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Cyanide and Compounds

Cyanide is a substance that is found in combination with other chemicals in the environment. Of these combinations (compounds), the ones people are most likely to come in contact with are hydrogen cyanide, sodium cyanide, and potassium cyanide. Hydrogen cyanide is a colorless gas or liquid with a faint, bitter almond odor. Sodium cyanide and potassium cyanide are both colorless solids that have a slight odor of bitter almonds in damp air. Cyanides are both man-made and naturally occurring substances. They are found in a number of foods and plants and are produced by certain bacteria, fungi, and algae. Very small amounts of cyanide, in the form of vitamin B12 (cyanocobalamin), are a necessary part of the human diet. Most of the cyanide found in the environment comes from industrial processes. Hydrogen cyanide is used mainly in the production of organic chemicals. Cyanide salts are used primarily in electroplating and metal treatment. Cyanide gained public attention when it was found to have caused the deaths of seven people who swallowed capsules contaminated with it.

2.1.1 Exposure Pathways

Humans can be exposed to cyanide from environmental, occupational, and consumer product sources. The single largest source of cyanide in air is from vehicle exhaust. Other sources of release to the air may include emissions from chemical processing industries, steel and iron industries, metallurgical industries, metal plating and finishing industries, and petroleum refineries. Cyanides may also be released from public waste incinerators, from waste disposed of in landfills, and during the use of cyanide-containing pesticides. When certain types of plastics, silk, wool, and paper are burned, cyanides are released. People who smoke tobacco take in larger amounts of cyanide than nonsmokers. The major sources of cyanide release to water are discharges from publicly owned wastewater treatment works, iron and steel production plants, and organic chemical industries. Much smaller amounts of cyanide may enter water through storm-water runoff in locations where cyanide-containing road salts are used. Groundwater can be contaminated by the movement of cyanide through soil from landfills. The largest sources of cyanide releases to soil are probably from the disposal of cyanide wastes in landfills and the use of cyanide-containing road salts. Cyanide has been found in at least 134 of the 1177 sites on the National Priorities List (NPL) of hazardous waste sites in the United States.

Workers may be exposed to cyanides in a wide variety of occupations including electroplating; metallurgy; metal cleaning; pesticide application; firefighting; steel manufacturing; gas works operations; manufacture of cyanides and some dyes, some pharmaceuticals, and some chelating agents; tannery work; blacksmithing; photoengraving; and photography. Cyanide also occurs naturally in a variety of fruits, vegetables, and grains. In the United States, only low levels of cyanide are taken in from eating food because foods with high cyanide levels are not a major part of the American diet.

2.1.2 Metabolism

Cyanide can enter the body when a person breathes air containing hydrogen cyanide vapor or dust containing cyanide compounds. This may be a common pathway of exposure for individuals who work with the chemical, and for those who smoke. It is probably also a common exposure pathway for those who live near industrial and commercial areas where large amounts of the compound are used or disposed of in waste sites. Cyanide can also enter the body when a person eats food or drinks water containing it. If cyanide is present at a waste site, it may get into underground water as it passes downward through the soil. It is not common for persons to be exposed to cyanide through skin contact, although it can enter the body this way. Skin exposure usually happens only in the workplace.

2.1.3 Health Effects

Cyanide in the form of vitamin B12 (cyanocobalamin) is needed as part of a healthy diet to prevent iron poor blood, or anemia. The effects of cyanide may vary from person to person depending upon things such as health, family traits, age, and sex. Exposure to high levels of cyanide for a short period harms the central nervous system, respiratory system, and cardiovascular system. Short-term exposure to high levels of cyanide can cause coma and/or death. Brief exposures to lower levels result in rapid, deep breathing; shortness of breath; convulsions; and loss of consciousness. These short-term effects go away with time because cyanide does not stay in the body. In some cases, quick medical treatment can revive a person who has been poisoned by cyanide. Skin contact with dust from certain cyanide compounds can cause skin irritation and ulcerations. People have developed damage to the nervous system and thyroid gland after eating food containing low levels of cyanide for a long time (months to years). Effects on the nervous system believed to be from long-term exposure to cyanide include deafness, vision problems, and loss of muscle coordination. Effects on the thyroid gland can cause cretinism (retarded physical and mental growth in children), or enlargement and overactivity of the gland. These effects have been seen in people who eat large amounts of cassava, a cyanide-containing vegetable, and who don't have enough iodine and other necessary nutrients in their diet. These effects have not been seen at levels of cyanide exposure usually found in foods in the United States. Some animal data show that cyanide may cause harm to the unborn offspring, but the studies are not complete enough to measure this effect. No evidence exists to tell if cyanide causes cancer. Inhalation exposure to cyanide causes rapid effects. Exposure of humans at a level of 110 ppm can cause death within 30 minutes to 1 hour. At a level of about 18 ppm, persons may have headaches, weakness, and nausea (after several hours of exposure). Hydrogen cyanide vapor has a smell of bitter almonds that some individuals can first smell at about 0.6 ppm. This smell will not alert everyone to the fact that hydrogen cyanide is in the air, because not all persons can smell hydrogen cyanide. Deaths in animals have been reported at exposure levels ranging from 20 ppm for 4.5 hours to 503 ppm for 5 minutes. Heart effects in rats have been reported following exposure at 200 ppm for 12.5 minutes. Little long-term exposure information is available. In humans exposed to cyanides in the workplace, effects on the thyroid gland and other health problems (breathing difficulty, headache, throat irritation, weakness, changes in taste and smell, abdominal pain, vomiting, and nervous instability) have been reported at levels of 6.4 to 10.3 ppm. Nervous system effects have been seen in dogs exposed to hydrogen cyanide at 45 ppm for 30 minutes a day for up to 22 weeks. Short-term exposures resulting from suicides and suicide attempts have been reported. The lowest amount eaten causing death was 0.56 mg/kg/day. There is no information showing that long-term exposure to cyanides in food or water causes health effects in humans. Harm to the nervous system and developing offspring has been seen in animals fed cyanides. A single dose of 3.4 mg/kg has caused death in animals. Rats died when a cyanide compound was placed directly into their stomachs daily for 90 days. A comparison of short-term and long-term animal studies shows that a single dose given all at one time can cause death, while higher levels of cyanides given in food over a longer time do not cause death. The reason for this may be that cyanides enter the body more slowly when given in food.

2.1.4 Regulations

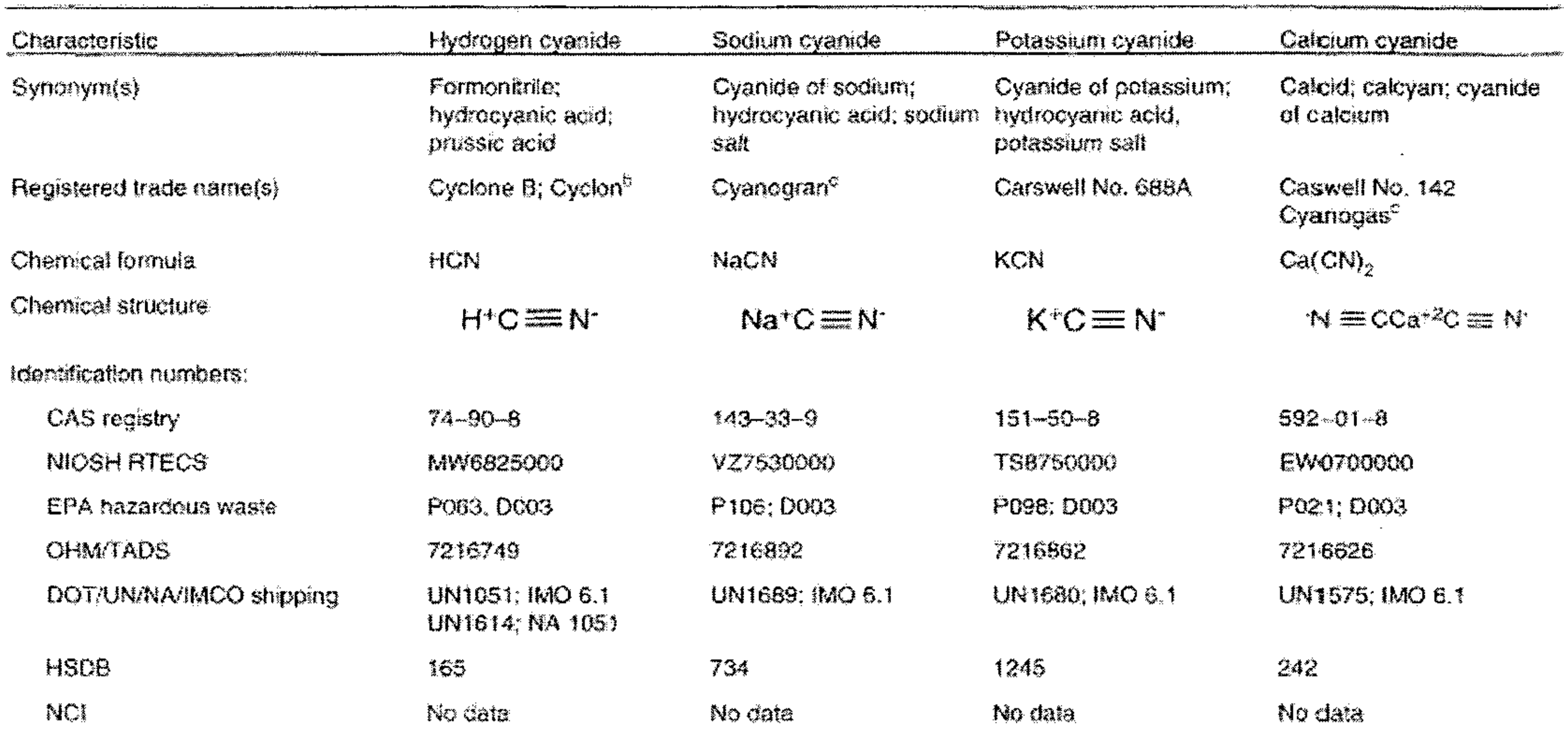
The government has made recommendations to limit the exposure of the general public to cyanide in food and the exposure of workers to cyanide in the workplace. Hydrogen cyanide is sometimes used to treat food after it is harvested to prevent pest damage. The Environmental Protection Agency (EPA) allows levels of cyanide in food ranging from 25 ppm in dried beans, peas, and nuts to 250 ppm in spices. Cyanide levels in the workplace are regulated by the Occupational Safety and Health Administration (OSHA). OSHA has a legally enforceable exposure limit of 5 milligrams of cyanide per cubic centimeter of air (mg/cm3) for cyanide and 11 mg/cm3 (or 10 ppm) hydrogen cyanide in air for an 8-hour workday, 40-hour workweek. The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to hydrogen cyanide and cyanide salts should not be more than 5 mg/m3 in air for a 10-minute sampling period.

2.1.5 Chemical Identity

Hydrogen cyanide is a toxic gas which enters the environment from both natural processes and human industrial activities. It may exist in polymeric forms. The cyanide compounds in which cyanide can be obtained as CN- are classified as simple and complex cyanides. Some simple cyanides are soluble in water (sodium cyanide, NaCN; potassium cyanide, KCN; calcium cyanide, Ca(CN)2), while others are sparingly soluble or almost insoluble (copper (I) cyanide, CuCN). Cyanogen chloride (CNCl) is a highly toxic gas that is soluble in water. At alkaline pH, CNC1 hydrolyzes to CNO- which has only limited toxicity. Alkaline chlorination of water containing cyanide produces cyanogen chloride. Thiocyanate (SCN-) is an oxidation product of cyanide, produced in the presence of sulfur.

2.2 Physical and Chemical Properties

Cyanides form strong complexes with many metals, particularly those of the transition series. One example of such complexation is the reaction of cyanide with iron in the formation of ferrocyanide and ferricyanide complexes. Solutions of ferrocyanides and ferricyanides can form hydrogen cyanide and cyanide ions when exposed to sunlight or ultraviolet radiation. Cyanogenic glycosides are cyanide compounds produced naturally in many plants. These glycosides produce hydrogen cyanide when hydrolyzed (Towill et al. 1978). Hydrogen cyanide has a pKa of 9.2 (Smith and Martell 1989); therefore, solutions of cyanide compounds in water (such as from sodium cyanide and potassium cyanide) can form hydrogen cyanide at acid and neutral pHs. Alkaline solutions with pH >12 are practical for preventing significant outgassing of hydrogen cyanide. Hydrogen cyanide is a fire hazard and may be explosive when an excess of a strong acid is added to confine hydrogen cyanide. Solutions of some cyanide compounds are not stable and may decompose upon exposure to air or light.



Characteristic	Hydrogen cyanide	Sodium cyanide	Potassium cyanide	Calcium cyanide
Synonym(s)	Formonitrile; hydrocyanic acid; prussic acid	Cyanide of sodium; hydrocyanic acid; sodium salt	Cyanide of potassium; hydrocyanic acid, potassium salt	Calcid; calcyan; cyanide of calcium
Registered trade name(s)	Cyclone B; Cyclon[b]	Cyanogran[c]	Carswell No. 688A	Caswell No. 142 Cyanogas[c]
Chemical formula	HCN	NaCN	KCN	$Ca(CN)_2$
Chemical structure	$H^{+}C\equiv N^{-}$	$Na^{+}C\equiv N^{-}$	$K^{+}C\equiv N^{-}$	$^{-}N\equiv CCa^{+2}C\equiv N^{-}$
Identification numbers:				
CAS registry	74–90–8	143–33–9	151–50–8	592–01–8
NIOSH RTECS	MW6825000	VZ7530000	TS8750000	EW0700000
EPA hazardous waste	P063, D003	P106; D003	P098; D003	P021; D003
OHM/TADS	7216749	7216892	7216862	7216626
DOT/UN/NA/IMCO shipping	UN1051; IMO 6.1 UN1614; NA 1051	UN1689; IMO 6.1	UN1680; IMO 6.1	UN1575; IMO 6.1
HSDB	165	734	1245	242
NCI	No data	No data	No data	No data

Table 2.1: Chemical Identity of Cyanide and Compounds

Characteristic	Copper(I) cyanide	Potassium silver cyanide	Cyanogen	Cyanogen chloride
Synonym(s)	Cuprous cyanide[c]; cupricin[c]	Potassium argento-cyanide; potassium dicyanoargentate	Carbon nitride; dicyanogen; ethanedinitrile	Chlorine cyanide; chlorocyan
Registered trade name(s)	AI3–28745	No data	No data	Caswell No. 267
Chemical formula	CuCN	$KAg(CN)_2$	$(CN)_2$	CNCl
Chemical structure	$Cu^{+}C\equiv N^{-}$	$K^{+}[Ag(CN)_2]^{-}$	$N\equiv C-C\equiv N$	$Cl-C\equiv N$
Identification numbers:				
CAS registry	544–92–3	506–61–6	460–19–5	506–77–4
NIOSH RTECS	GL7150000	TT5775000	GT1925000	GT2275000
EPA hazardous waste	P029; D003	P099; D003; D011	P031; D003	P033; D003
OHM/TADS	No data	No data	7216656	7216658
DOT/UN/NA/IMCO shipping	UN1587; IMO 6.1	No data	UN1026; IMO 2.3	UN1589; IMO 2.3
HSDB	1438	6053	2130	917
NCI	No data	No data	No data	No data

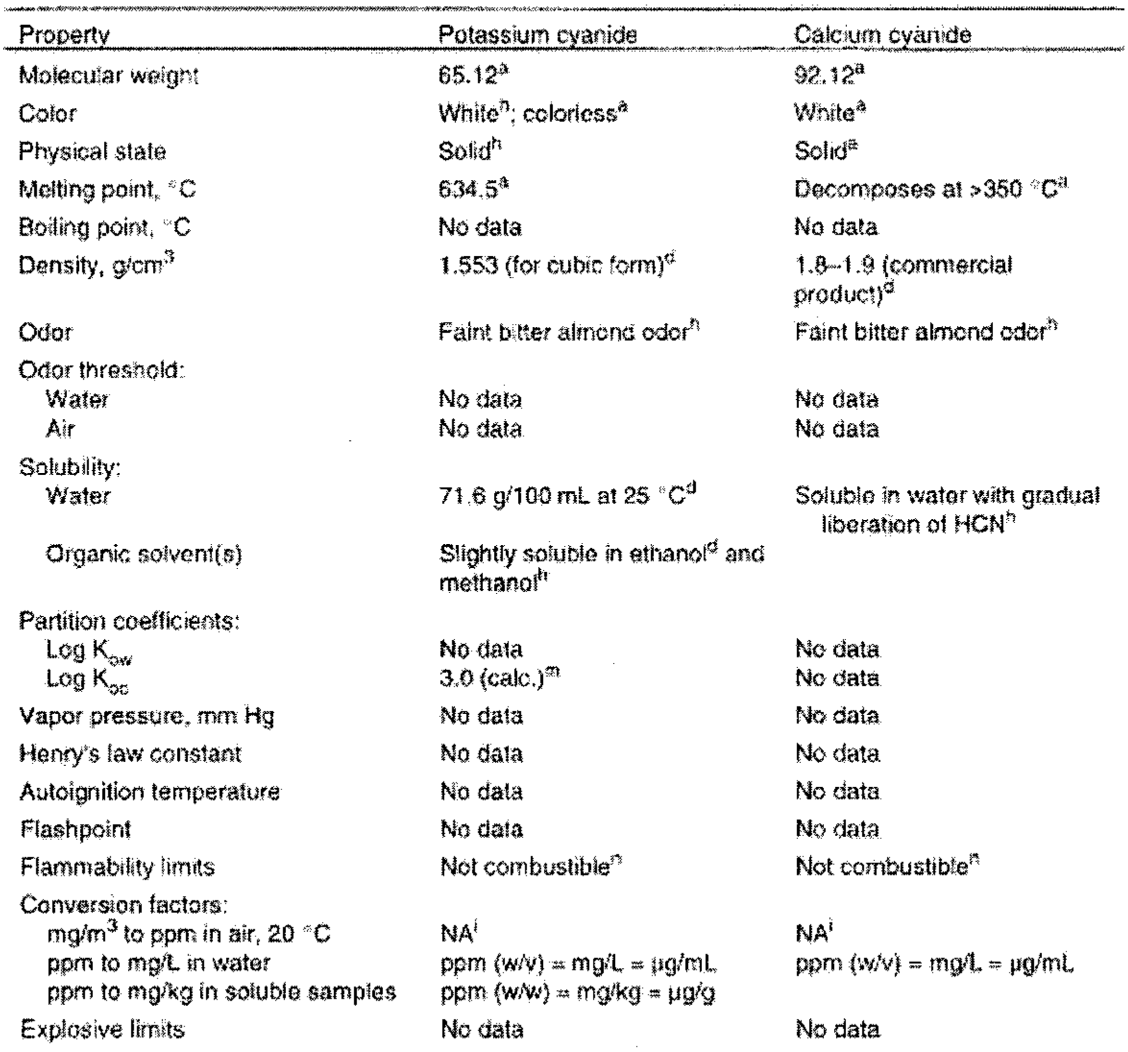
Table 2.1: Chemical Identity of Cyanide and Compounds (continued)

Characteristic	Ammonium thiocyanate
Synonym(s)	Thiocyanic acid, ammonium salt; ammonium rhodanide; ammonium sulfocyanate[c]
Registered trade name(s)	Trans-Aid[b]
Chemical formula	$NH_4^+S-C\equiv N^-$
Chemical structure	NH_4SCN
Identification numbers:	
CAS registry	1762-95-4
NIOSH RTECS	XK7875000
EPA hazardous waste	No data
OHM/TADS	721218
DOT/UN/NA/IMCO shipping	NA9092
HSDB	701
NCI	No data

[a] All data are from HSDB 1996 unless otherwise noted.
[b] Farm Chemicals Handbook 1983
[c] Merck 1989

CAS = Chemical Abstracts Service; DOT/UN/NA/IMO = Dept. of Transportation/United Nations/North America/International Maritime Dangerous Goods Code; EPA = Environmental Protection Agency; HSDB = Hazardous Substances Data Bank; NCI = National Cancer Institute; NIOSH = National Institute for Occupational Safety and Health; OHM/TADS = Oil and Hazardous Materials/Technical Assistance Data System; RTECS = Registry of Toxic Effects of Chemical Substances

Table 2.1: Chemical Identity of Cyanide and Compounds (continued)



Property	Potassium cyanide	Calcium cyanide
Molecular weight	65.12[a]	92.12[a]
Color	White[h]; colorless[a]	White[a]
Physical state	Solid[h]	Solid[a]
Melting point, °C	634.5[a]	Decomposes at >350 °C[d]
Boiling point, °C	No data	No data
Density, g/cm^3	1.553 (for cubic form)[d]	1.8–1.9 (commercial product)[d]
Odor	Faint bitter almond odor[h]	Faint bitter almond odor[h]
Odor threshold:		
Water	No data	No data
Air	No data	No data
Solubility:		
Water	71.6 g/100 mL at 25 °C[d]	Soluble in water with gradual liberation of HCN[h]
Organic solvent(s)	Slightly soluble in ethanol[d] and methanol[h]	
Partition coefficients:		
Log K_{ow}	No data	No data
Log K_{oc}	3.0 (calc.)[m]	No data
Vapor pressure, mm Hg	No data	No data
Henry's law constant	No data	No data
Autoignition temperature	No data	No data
Flashpoint	No data	No data
Flammability limits	Not combustible[h]	Not combustible[h]
Conversion factors:		
mg/m^3 to ppm in air, 20 °C	NA[i]	NA[i]
ppm to mg/L in water	ppm (w/v) = mg/L = μg/mL	ppm (w/v) = mg/L = μg/mL
ppm to mg/kg in soluble samples	ppm (w/w) = mg/kg = μg/g	
Explosive limits	No data	No data

Figure 2.2: Physical and Chemical Properties for Cyanide and Compounds

Property	Potassium silver cyanide	Cyanogen
Molecular weight	199.01[h]	52.04[a]
Color	White[h]	Colorless[a]
Physical state	Solid[h]	Gas[a]
Melting point, °C	No data	–27.9[a]
Boiling point, °C	No data	–20.7[a]
Density, g/cm^3	2.36[a]	0.9577 at –21.17 °C[a]
Odor	No data	Almond–like odor[h]
Odor threshold:		
Water	No data	No data
Air	No data	230 ppm; irritating at 15 ppm[g]
Solubility:		
Water	Soluble[h]	450 cc/100 cc (20 °C)[a]
Organic solvent(s)	Slightly soluble in ethanol[a]	Soluble in ethanol and ethyl ether[a]
Partition coefficients:		
Log K_{ow}	No data	No data
Log K_{oc}	No data	No data
Vapor pressure, mm Hg	No data	3,800 at 20 °C[j]
Henry's law constant	No data	No data
Autoignition temperature	No data	No data
Flashpoint	No data	No data
Flammability limits	No data	6.6 – 32% in air[h]
Conversion factors:		
mg/m^3 to ppm in air, 20 °C	NA[i]	1 mg/m^3 = 0.462 ppm
ppm to mg/L in water	ppm (w/v) = mg/L = µg/mL	ppm (w/v) = mg/L = µg/mL
ppm to mg/kg in soluble samples	ppm (w/w) = mg/kg = µg/g	ppm (w/w) = mg/kg = µg/g
Explosive limits	No data	No data

Figure 2.2: Physical and Chemical Properties for Cyanide and Compounds (continued)

2.3 Ion Exchange Separation Process

2.2.1 Mechanism of Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most plating process water is used to cleanse the surface of the parts after each process bath. To maintain quality standards, the level of dissolved solids in the rinse water must be regulated. Fresh water added to the rinse tank accomplishes this purpose, and the overflow water is treated to remove pollutants and then discharged. As the metal salts, acids, and bases used in metal finishing are primarily inorganic compounds, they are ionized in water and could be removed by contact with ion exchange resins. In a water deionization process, the resins exchange hydrogen ions (H^+) for the positively charged ions (such as nickel. copper, and sodium) and hydroxyl ions (OH^-) for negatively charged sulfates, chromates and chlorides. Because the quantity of H^+ and OH ions is balanced, the result of the ion exchange treatment is relatively pure, neutral water.

2.2.2 Process Reactions

Ion exchange reactions are stoichiometric and reversible, and in that way they are similar to other solution phase reactions. For example:

$$NiSO_4 + Ca(OH)_2 = Ni(OH)_2 + CaSO_4 \qquad (1)$$

In this reaction, the nickel ions of the nickel sulfate ($NiSO_4$) are exchanged for the calcium ions of the calcium hydroxide [$Ca(OH)_2$] molecule. Similarly, a resin with hydrogen ions available for exchange will exchange those ions for nickel ions from solution. The reaction can be written as follows:

$$2(R\text{-}SO_3H) + NiSO_4 = (R\text{-}SO_3)_2Ni + H_2SO_4 \qquad (2)$$

R indicates the organic portion of the resin and SO3 is the immobile portion of the ion active group. Two resin sites are needed for nickel ions with a plus 2 valence (Ni+2). Trivalent ferric ions would require three resin sites. As shown, the ion exchange reaction is reversible. The degree the reaction proceeds to the right will depend on the resins preference or selectivity, for nickel ions compared with its preference for hydrogen ions.

2.2.3 Resin Selection

$$R\text{-}A++B+ \;=\; R\text{--}B++A+ \qquad (3)$$

The selectivity of a resin for a given ion is measured by the selectivity coefficient, K which in its simplest form for the reaction is expressed as: K = (concentration of B+ in resin/concentration of A+ in resin) X (concentration of A+ in solution/concentration of B+ in solution). The selectivity coefficient expresses the relative distribution of the ions when a resin in the A+ form is placed in a solution containing B+ ions. Table 1 gives the selectivity's of strong acid and strong base ion exchange resins for various ionic compounds. It should be pointed out that the selectivity coefficient is not constant but varies with changes in solution conditions. It does provide a means of determining what to expect when various ions are involved. As indicated in Table 1, strong acid resins have a preference for nickel over hydrogen. Despite this preference, the resin can be converted back to the hydrogen form by contact with a concentrated solution of sulfuric acid (H2SO4):

$$(R\text{--}SO_4)_2Ni + H_2SO_4 \text{ -> } 2(R\text{-}SO3H) + NiSO_4 \quad (4)$$

This step is known as regeneration. In general terms, the higher the preference a resin exhibits for a particular ion, the greater the exchange efficiency in terms of resin capacity for removal of that ion from solution. Greater preference for a particular ion, however, will result in increased consumption of chemicals for regeneration. Resins currently available exhibit a range of selectivity's and thus have broad application. As an example for a strong acid resin, the relative preference for divalent calcium ions (Ca^{+2}) over divalent copper ions (Cu^{+2}) is approximately 1.5 to 1. For a heavy-metal-selective resin the preference is reversed and favors copper by a ratio of 2.300 to 1.

Strong Acid Cation Exchanger	**Strong Base Anion Exchanger**
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia Sodium	
Hydrogen	

Table 2.3: Selectivity of ion Exchange Resins in Order of Decreasing Preference

2.4 Resin Type

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

2.4.1 Strong Acid Cation Resins

Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO3H) and salt (R-SO3Na) form. They can convert a metal salt to the corresponding acid by the reaction:

$$2(R\text{-}SO_3H) + NiCl_2 \dashrightarrow (R\text{-}SO_4),Ni + 2HCI \qquad (5)$$

The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na+ and H+ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be convened to the sodium form with a sodium chloride solution. For Equation 5 hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride (NiCl,) solution.

2.4.2 Weak Acid Cation Resins

In a weak acid resin the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO_3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH. Figure 1 shows that a typical weak acid resin has limited capacity below a pH of 6.0 making it unsuitable for deionizing acidic metal finishing wastewater.

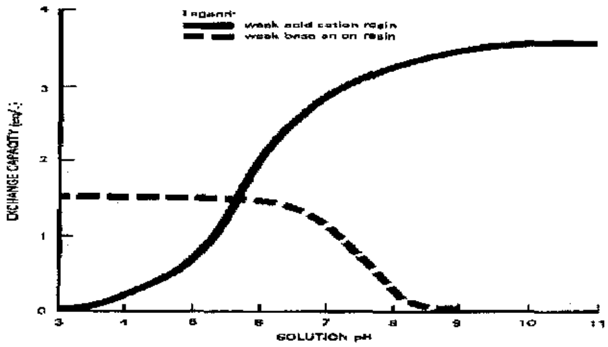
2.4.3 Strong Base Anion Resins

Like strong acid resins. strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH) form for water deionization. Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form. They will react with anions in solution and can convert an acid solution to pure water:

$$R\text{--}NH_3OH + HCl \rightarrow R\text{-}NH_3Cl + HOH \qquad (6)$$

2.4.4 Weak Base Anion Resins

Weak base resins are like weak acid resins. in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 (Figure 2.1). These resins merely absorb strong acids: they cannot split salts.



SOURCE: Adapted from Schweitzer, P. A., *Handbook of Separation Techniques for Chemical Engineers*, New York NY, McGraw-Hill, 1979.

Figure 2.1: Exchange Capacity of Weak Acid Cation and Weak Base Anion Resins as a Function of solution pH

In an ion exchange wastewater deionization unit, the wastewater would pass first through a bed of strong acid resin. Replacement of the metal cations (Ni^{+2} Cu^{+2}) with hydrogen ions would lower the solution pH. The anions (SO4^{-2}. Cl^{-}) can then be removed with a weak base resin because the entering wastewater will normally be acidic and weak base resins sorb acids. Weak base resins are preferred over strong base resins because they require less regenerant chemical. A reaction between the resin in the free base form and HCl would proceed as follows:

$$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3Cl \qquad (7)$$

The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, regeneration needs only to neutralize the absorbed acid: it need not provide hydroxide ions. Less expensive weakly basic reagents such as ammonia (NH3) or sodium carbonate can be employed.

2.4.5 Heavy-Metal-Selective Chelating Resins

Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact, the functional group used in these resins is an EDTAa compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

The high degree of selectivity for heavy metals permits separation of these ionic compounds from solutions containing high background levels of calcium, magnesium, and sodium ions. A chelating resin exhibits greater selectivity for heavy metals in its sodium form than in its hydrogen form. Regeneration properties are similar to those of a weak acid resin; the chelating resin can be converted to the hydrogen form with slightly greater than stoichiometric doses of acid because of the fortunate tendency of the heavy metal complex to become less stable under low pH conditions. Potential applications of the chelating resin include polishing to lower the heavy metal concentration in the effluent from a hydroxide treatment process or directly removing toxic heavy metal cations from wastewaters containing a high concentration of nontoxic, multivalent cations.

Characteristic	Hydrogen cyanide	Sodium cyanide	Potassium cyanide	Calcium cyanide
Synonym(s)	Formonitrile; hydrocyanic acid; prussic acid	Cyanide of sodium; hydrocyanic acid; sodium salt	Cyanide of potassium; hydrocyanic acid, potassium salt	Calcid; calcyan; cyanide of calcium
Registered trade name(s)	Cyclone B; Cyclon[b]	Cyanogran[c]	Carswell No. 688A	Caswell No. 142 Cyanogas[c]
Chemical formula	HCN	NaCN	KCN	$Ca(CN)_2$
Chemical structure	$H^+C\equiv N^-$	$Na^+C\equiv N^-$	$K^+C\equiv N^-$	$^-N\equiv CCa^{+2}C\equiv N^-$
Identification numbers:				
CAS registry	74–90–8	143–33–9	151–50–8	592–01–8
NIOSH RTECS	MW6825000	VZ7530000	TS8750000	EW0700000
EPA hazardous waste	P063, D003	P106; D003	P098; D003	P021; D003
OHM/TADS	7216749	7216892	7216862	7216626
DOT/UN/NA/IMCO shipping	UN1051; IMO 6.1 UN1614; NA 1051	UN1689; IMO 6.1	UN1680; IMO 6.1	UN1575; IMO 6.1
HSDB	165	734	1245	242
NCI	No data	No data	No data	No data

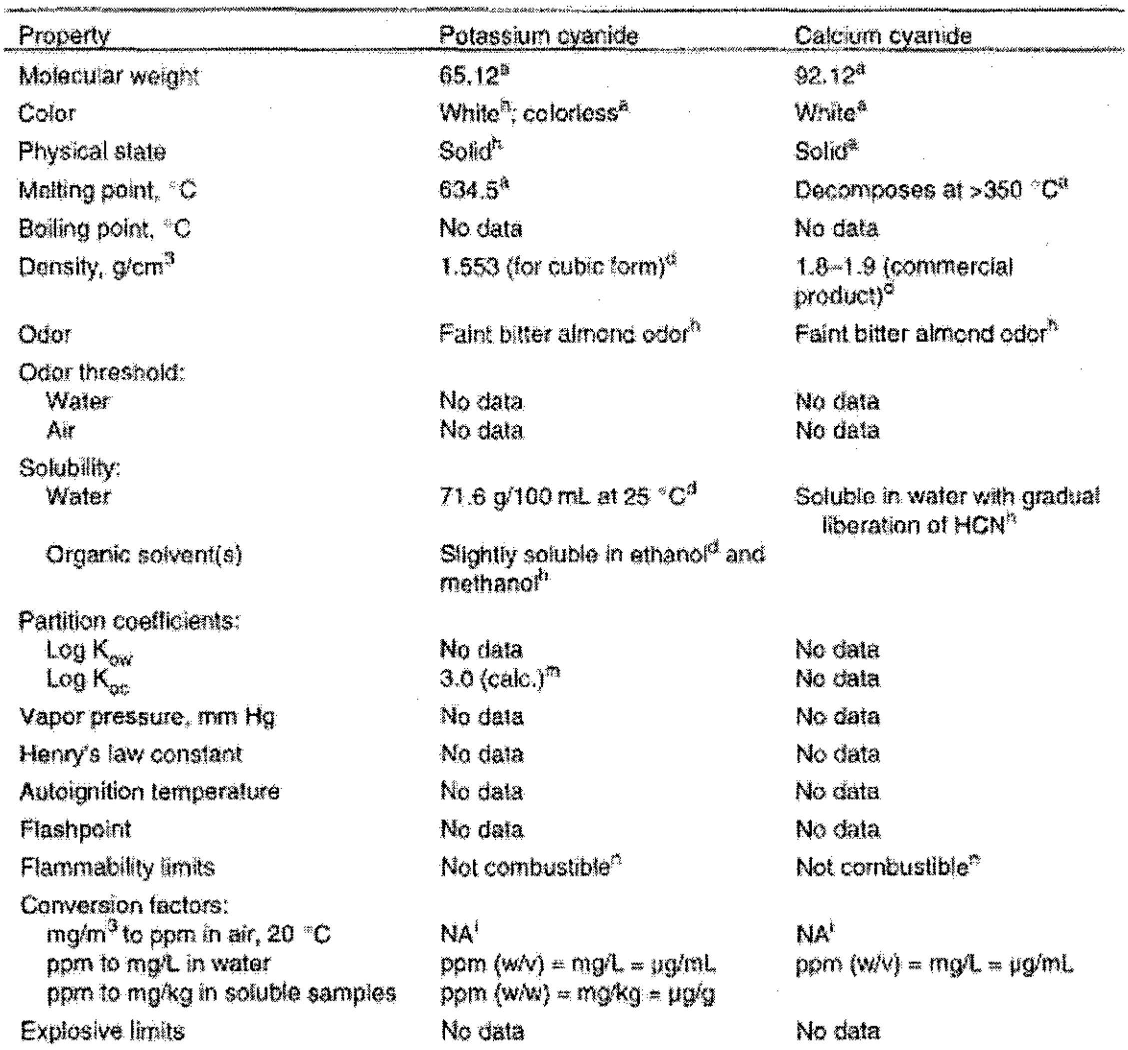
Table 2.1: Chemical Identity of Cyanide and Compounds

Characteristic	Ammonium thiocyanate
Synonym(s)	Thiocyanic acid, ammonium salt; ammonium rhodanide; ammonium sulfocyanate[c]
Registered trade name(s)	Trans-Aid[b]
Chemical formula	$NH_4^+S-C\equiv N^-$
Chemical structure	NH_4SCN
Identification numbers:	
CAS registry	1762-95-4
NIOSH RTECS	XK7875000
EPA hazardous waste	No data
OHM/TADS	721218
DOT/UN/NA/IMCO shipping	NA9092
HSDB	701
NCI	No data

[a] All data are from HSDB 1996 unless otherwise noted.
[b] Farm Chemicals Handbook 1983
[c] Merck 1989

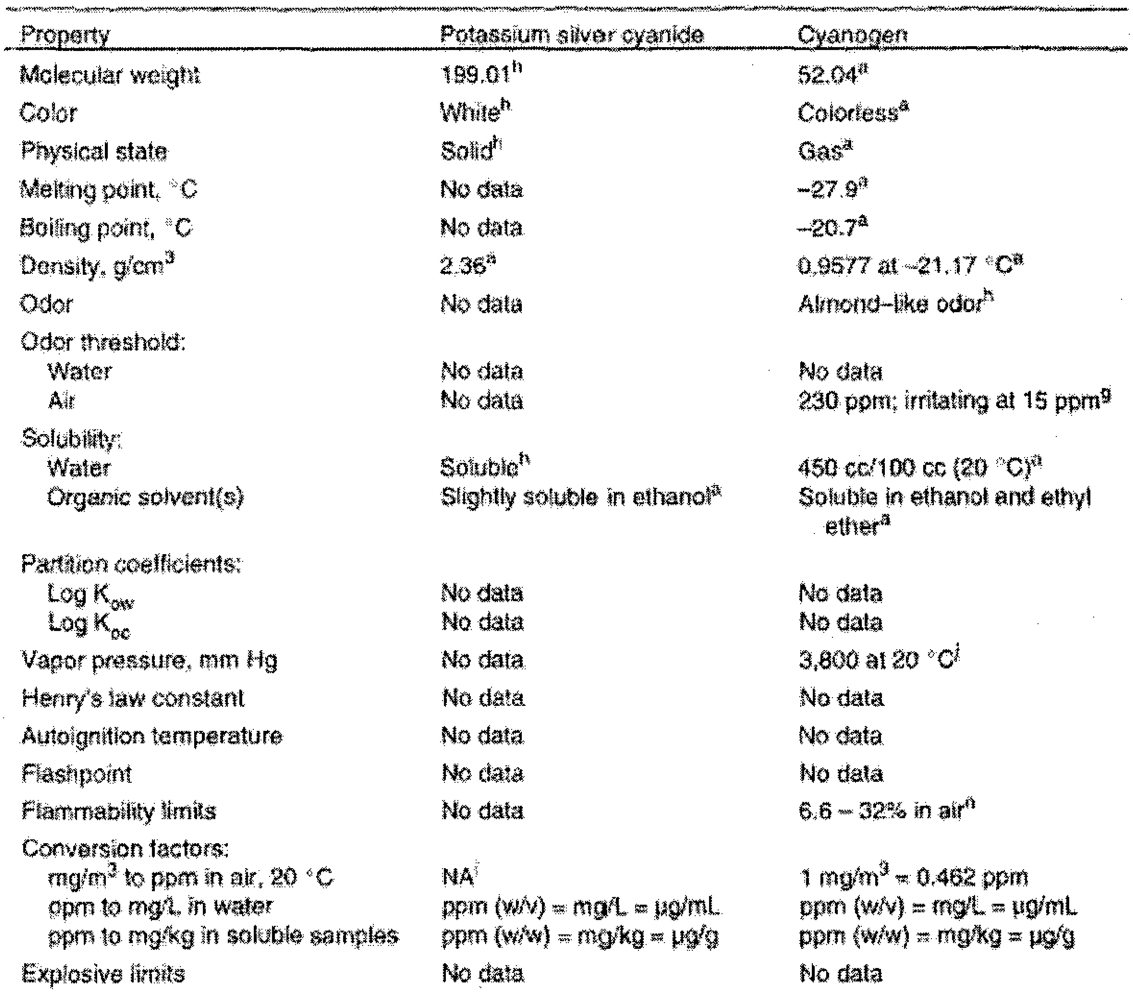
CAS = Chemical Abstracts Service; DOT/UN/NA/IMO = Dept. of Transportation/United Nations/North America/International Maritime Dangerous Goods Code; EPA = Environmental Protection Agency; HSDB = Hazardous Substances Data Bank; NCI = National Cancer Institute; NIOSH = National Institute for Occupational Safety and Health; OHM/TADS = Oil and Hazardous Materials/Technical Assistance Data System; RTECS = Registry of Toxic Effects of Chemical Substances

Table 2.1: Chemical Identity of Cyanide and Compounds (continued)



Property	Potassium cyanide	Calcium cyanide
Molecular weight	65.12[a]	92.12[a]
Color	White[h]; colorless[a]	White[a]
Physical state	Solid[h]	Solid[a]
Melting point, °C	634.5[a]	Decomposes at >350 °C[d]
Boiling point, °C	No data	No data
Density, g/cm^3	1.553 (for cubic form)[d]	1.8–1.9 (commercial product)[d]
Odor	Faint bitter almond odor[h]	Faint bitter almond odor[h]
Odor threshold:		
Water	No data	No data
Air	No data	No data
Solubility:		
Water	71.6 g/100 mL at 25 °C[d]	Soluble in water with gradual liberation of HCN[h]
Organic solvent(s)	Slightly soluble in ethanol[d] and methanol[h]	
Partition coefficients:		
Log K_{ow}	No data	No data
Log K_{oc}	3.0 (calc.)[m]	No data
Vapor pressure, mm Hg	No data	No data
Henry's law constant	No data	No data
Autoignition temperature	No data	No data
Flashpoint	No data	No data
Flammability limits	Not combustible[h]	Not combustible[h]
Conversion factors:		
mg/m^3 to ppm in air, 20 °C	NA[i]	NA[i]
ppm to mg/L in water	ppm (w/v) = mg/L = µg/mL	ppm (w/v) = mg/L = µg/mL
ppm to mg/kg in soluble samples	ppm (w/w) = mg/kg = µg/g	
Explosive limits	No data	No data

Figure 2.2: Physical and Chemical Properties for Cyanide and Compounds



Property	Potassium silver cyanide	Cyanogen
Molecular weight	199.01[h]	52.04[a]
Color	White[h]	Colorless[a]
Physical state	Solid[h]	Gas[a]
Melting point, °C	No data	–27.9[a]
Boiling point, °C	No data	–20.7[a]
Density, g/cm^3	2.36[a]	0.9577 at –21.17 °C[a]
Odor	No data	Almond–like odor[h]
Odor threshold:		
Water	No data	No data
Air	No data	230 ppm; irritating at 15 ppm[g]
Solubility:		
Water	Soluble[h]	450 cc/100 cc (20 °C)[a]
Organic solvent(s)	Slightly soluble in ethanol[a]	Soluble in ethanol and ethyl ether[a]
Partition coefficients:		
Log K_{ow}	No data	No data
Log K_{oc}	No data	No data
Vapor pressure, mm Hg	No data	3,800 at 20 °C[j]
Henry's law constant	No data	No data
Autoignition temperature	No data	No data
Flashpoint	No data	No data
Flammability limits	No data	6.6 – 32% in air[h]
Conversion factors:		
mg/m^3 to ppm in air, 20 °C	NA[i]	1 mg/m^3 = 0.462 ppm
ppm to mg/L in water	ppm (w/v) = mg/L = µg/mL	ppm (w/v) = mg/L = µg/mL
ppm to mg/kg in soluble samples	ppm (w/w) = mg/kg = µg/g	ppm (w/w) = mg/kg = µg/g
Explosive limits	No data	No data

Figure 2.2: Physical and Chemical Properties for Cyanide and Compounds (continued)

2.3 Ion Exchange Separation Process

2.2.1 Mechanism of Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most plating process water is used to cleanse the surface of the parts after each process bath. To maintain quality standards, the level of dissolved solids in the rinse water must be regulated. Fresh water added to the rinse tank accomplishes this purpose, and the overflow water is treated to remove pollutants and then discharged. As the metal salts, acids, and bases used in metal finishing are primarily inorganic compounds, they are ionized in water and could be removed by contact with ion exchange resins. In a water deionization process, the resins exchange hydrogen ions (H^+) for the positively charged ions (such as nickel. copper, and sodium) and hydroxyl ions (OH^-) for negatively charged sulfates, chromates and chlorides. Because the quantity of H^+ and OH ions is balanced, the result of the ion exchange treatment is relatively pure, neutral water.

2.2.2 Process Reactions

Ion exchange reactions are stoichiometric and reversible, and in that way they are similar to other solution phase reactions. For example:

$$NiSO_4 + Ca(OH)_2 = Ni(OH)_2 + CaSO_4 \qquad (1)$$

In this reaction, the nickel ions of the nickel sulfate ($NiSO_4$) are exchanged for the calcium ions of the calcium hydroxide [$Ca(OH)_2$] molecule. Similarly, a resin with hydrogen ions available for exchange will exchange those ions for nickel ions from solution. The reaction can be written as follows:

$$2(R\text{-}SO_3H) + NiSO_4 = (R\text{-}SO_3)_2Ni + H_2SO_4 \qquad (2)$$

R indicates the organic portion of the resin and SO3 is the immobile portion of the ion active group. Two resin sites are needed for nickel ions with a plus 2 valence (Ni+2). Trivalent ferric ions would require three resin sites. As shown, the ion exchange reaction is reversible. The degree the reaction proceeds to the right will depend on the resins preference or selectivity, for nickel ions compared with its preference for hydrogen ions.

2.2.3 Resin Selection

$$R\text{-}A{+}{+}B{+} \quad = \quad R\text{-}{-}B{+}{+}A{+} \qquad (3)$$

The selectivity of a resin for a given ion is measured by the selectivity coefficient, K which in its simplest form for the reaction is expressed as: K = (concentration of B+ in resin/concentration of A+ in resin) X (concentration of A+ in solution/concentration of B+ in solution). The selectivity coefficient expresses the relative distribution of the ions when a resin in the A+ form is placed in a solution containing B+ ions. Table 1 gives the selectivity's of strong acid and strong base ion exchange resins for various ionic compounds. It should be pointed out that the selectivity coefficient is not constant but varies with changes in solution conditions. It does provide a means of determining what to expect when various ions are involved. As indicated in Table 1, strong acid resins have a preference for nickel over hydrogen. Despite this preference, the resin can be converted back to the hydrogen form by contact with a concentrated solution of sulfuric acid (H2SO4):

$$(R\text{--}SO_4)_2Ni + H_2SO_4 \text{ -> } 2(R\text{-}SO3H) + NiSO_4 \quad (4)$$

This step is known as regeneration. In general terms, the higher the preference a resin exhibits for a particular ion, the greater the exchange efficiency in terms of resin capacity for removal of that ion from solution. Greater preference for a particular ion, however, will result in increased consumption of chemicals for regeneration. Resins currently available exhibit a range of selectivity's and thus have broad application. As an example for a strong acid resin, the relative preference for divalent calcium ions (Ca^{+2}) over divalent copper ions (Cu^{+2}) is approximately 1.5 to 1. For a heavy-metal-selective resin the preference is reversed and favors copper by a ratio of 2.300 to 1.

Strong Acid Cation Exchanger	Strong Base Anion Exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia Sodium	
Hydrogen	

Table 2.3: Selectivity of ion Exchange Resins in Order of Decreasing Preference

2.4 Resin Type

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

2.4.1 Strong Acid Cation Resins

Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO3H) and salt (R-SO3Na) form. They can convert a metal salt to the corresponding acid by the reaction:

$$2(R\text{-}SO_3H) + NiCl_2 \text{ --> } (R\text{-}SO_4),Ni + 2HCl \qquad (5)$$

The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na+ and H+ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be convened to the sodium form with a sodium chloride solution. For Equation 5 hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride (NiCl,) solution.

2.4.2 Weak Acid Cation Resins

In a weak acid resin the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO_3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH. Figure 1 shows that a typical weak acid resin has limited capacity below a pH of 6.0 making it unsuitable for deionizing acidic metal finishing wastewater.

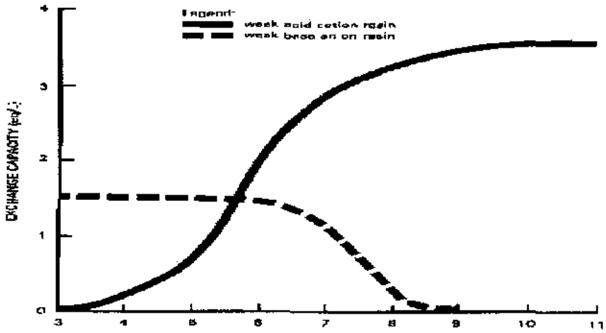
2.4.3 Strong Base Anion Resins

Like strong acid resins. strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH) form for water deionization. Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form. They will react with anions in solution and can convert an acid solution to pure water:

$$R\text{--}NH_3OH + HCl \rightarrow R\text{-}NH_3Cl + HOH \qquad (6)$$

2.4.4 Weak Base Anion Resins

Weak base resins are like weak acid resins. in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 (Figure 2.1). These resins merely absorb strong acids: they cannot split salts.



SOURCE: Adapted from Schweitzer, P. A., *Handbook of Separation Techniques for Chemical Engineers*. New York NY, McGraw-Hill, 1979.

Figure 2.1: Exchange Capacity of Weak Acid Cation and Weak Base Anion Resins as a Function of solution pH

In an ion exchange wastewater deionization unit, the wastewater would pass first through a bed of strong acid resin. Replacement of the metal cations (Ni^{+2} Cu^{+2}) with hydrogen ions would lower the solution pH. The anions (SO4^{-2}. Cl^{-}) can then be removed with a weak base resin because the entering wastewater will normally be acidic and weak base resins sorb acids. Weak base resins are preferred over strong base resins because they require less regenerant chemical. A reaction between the resin in the free base form and HCl would proceed as follows:

$$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3Cl \qquad (7)$$

The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, regeneration needs only to neutralize the absorbed acid: it need not provide hydroxide ions. Less expensive weakly basic reagents such as ammonia (NH3) or sodium carbonate can be employed.

2.4.5 Heavy-Metal-Selective Chelating Resins

Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact, the functional group used in these resins is an EDTAa compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

The high degree of selectivity for heavy metals permits separation of these ionic compounds from solutions containing high background levels of calcium, magnesium, and sodium ions. A chelating resin exhibits greater selectivity for heavy metals in its sodium form than in its hydrogen form. Regeneration properties are similar to those of a weak acid resin; the chelating resin can be converted to the hydrogen form with slightly greater than stoichiometric doses of acid because of the fortunate tendency of the heavy metal complex to become less stable under low pH conditions. Potential applications of the chelating resin include polishing to lower the heavy metal concentration in the effluent from a hydroxide treatment process or directly removing toxic heavy metal cations from wastewaters containing a high concentration of nontoxic, multivalent cations.

CHAPTER 3

METHODOLOGY

3.1 Separation of Cyanide from Wastewater Using Ion Exchange Reaction Process – Qualitative Test

3.1.1 Artificial Wastewater

In Malaysia, the concern upon Cyanide content in wastewater was yet to be addressed due to the growth of industries which producing Cyanide as product effluent still under control. Therefore, the wastewater sample for the study would be a quit big problem to be collected via industries wastewater in Malaysia. Furthermore, the study was not being addressed either to any particular industries or third parties which resulted in difficulties to collect the required wastewater sample. Though, it was decided that the wastewater sample for the study been prepared in University Teknologi PETRONAS. Preparation of the artificial wastewater also included in one of the study objectives. Due to the study concern on the cyanide removal, the preparation of artificial wastewater would contribute to the mixing of an amount of cyanide to the wastewater sample. Pure cyanide is hardly available at site because of its hazards and dangers to the humans and environment. Though Potassium Cyanide was considered as the best replacement in preparing the desired artificial wastewater. According to the study made in Turkey early February 1994, the cyanide content found in wastewater was around 1000 to 1500 mg/L.

PUSAT SUMBER MAKLUMAT
UNIVERSITI TEKNOLOGI PETRONAS

The value has been taken as a base for this study due to unavailable data in Malaysia wastewater accordingly.

3.1.2 SOLTEQ Ion Exchange Unit (*Model: TR02)*

SOLTEQ Ion Exchange Unit (*Mode: TR02)* assembled in University Teknologi PETRONAS Wastewater Laboratory under supervision of Chemical Engineering department is designed for the study of the uses of ion exchange resins for water softening, decationization, deionization as well as demineralization process. The unit also allowed for the study on the adsorption capacity of ion exchange resins used. The unit consists of a diaphragm type-metering pump with capacity of 5 L/hr @ 10 bar delivering 50 watts power operated under electrical specification of 240VAC/1ph/50Hz, Liquid flowmeter ranges from 0 to 80 ml/min, two (2) removable as well as interchangeable vertical tubes made of clear acrylic containing respective cation and anion resins with 600mm and 300mm height for large and small columns respectively and internal diameter of 20mm, two (2) units of conductivity meter and deionizer. Please refer to Figure 3.1, 3.2 and 3.3 in Appendix 3-1 to view on the ion exchange unit used.

3.1.2 Ion Exchange Resin

Ion exchangers are resins. These resins are polymers that have cross-linking, which is basically the amount of connections between long carbon chains in a polymer. The resin has active groups in the form of electrically charged sites. At these sites, ions, being electrically charged one way or another, may be replaced by other ions if it is favorable. Two key factors determine the effectiveness of a given ion exchange resin: favorability of any given ion, and the number of active sites available for this exchange. In order to maximize the active sites, significant surface areas are generally desirable. The active sites are generally one of a few types of functional groups that can exchange hydrogen or hydroxyl ions for whatever ion is desired to be exchanged. Frequently, the resins come in the form of porous beads.

Cross-linking is usually on the order of .5 to .15 percent, and cross-linking is usually accomplished adding divinyl benzene to the reaction mixture during production of the resin. The size of the particles also plays a role in the utility of the resin. Smaller particles usually are more effective, due to the increased surface area, but cause large head losses that drive up pump equipment and energy costs. Large particles are not as effective, but are cheaper to operate. Temperature and pH also affect the effectiveness of the ion exchange process, since pH is inherently tied to the number of ions available for exchange, and temperature governs the kinetics of the process. The rate-limiting step is not always the same, and how temperature's role in ion exchange for maximizing the process is still not thoroughly understood.

Regeneration of the resin is also a feature of ion exchange, in which the resin can be flushed free of the newly-exchanged ions in favor of it's original structure. The regeneration is usually desirable once a breakthrough point has been reached, which is the point at which most of the active sites have been used and the ion exchange is no longer effective. With regeneration, the same resin beads can be used over and over again, and the ions that we are looking to get out of the system can be concentrated in the backwash effluent, which is just a term for the fluid used to regenerate the ion exchanger.

For this study of cyanide removal, the ion exchange process was dealt with a particular type of resin named LEWATIT Monoplus S 1467 (C240-NS) from BAYER. C240-NS is a neutral (pH = 7) resin. In fact this is the only anion resin available in University Teknologi PETRONAS which is the best to be applied for the desired separation using ion exchange the one of its kinds although deanionization required strong base resin. Please refer to Figure 3.4 and in Appendix 3-2.

3.1.3 Coagulation and Flocculation

Coagulation and flocculation has been carried out in this study to consolidate suspended and colloidal impurities for the test water to observe on its effect to the ion exchange process. The test water is coagulated and flocculated in two(2) different step with two(2) different amount of coagulant (Aluminium Sulphate, $Al_2(SO_3)_4$) which are 10g and 20g respectively and both were stirred on the jar test at an identical speed set that thought to be most appropriate. The coagulated and flocculated test water is then applied to the ion exchange unit process operation.

3.2 Analysis on the Cyanide Content after Ion Exchange Treatment – Quantitative Test

Analysis on the after treatment artificial wastewater samples for cyanide content could be conducted in several testing method which available in University Teknologi PETRONAS. Theoretically the equipments that capable in analyzing cyanide content in wastewater available in University Teknologi PETRONAS are Atomic Absorption Spectroscopy (AAS), Gas Chromatography/Mass Spectroscopy (GCMS) and HACH kit water analysis. Complex titration or Photometric Titrations also could be an alternative to those equipments stated earlier but with complexing agents present.

Atomic Absorption Spectroscopy (AAS) and Gas Chromatography/Mass Spectroscopy (GCMS) in UTP were not capable to carry out the test due to no cyanide standard on site. The complex titrations was impossible to be carried out when the complexing agent; barbiturate acid was banned by the Malaysia Department of Environment (DOE). The only left alternatives was HACH kit which then been agreed to be used for the cyanide quantitative test.

3.2.1 HACH kit water analysis procedure

Five samples from five runs of the experiment have been analyzed using HACH kit water analysis. During the test period water bath has been used to maintain the optimum temperature of the reaction (25°C). Sample at less than 23°C require longer reaction times, and samples at greater than 25 ° C yield low results. Sample bottles were left free from fingerprint plus all samples have been treated by acid distillation. After all the samples qualitatively ready for test, Hach Programs has been activated and program of 160 Cyanide selected. Then start button was pressed. The round sample cell is filled with 10 mL sample then one CyaniVer 3 Cyanide Reagent Powder Pillow is added to the cell and capped. Sample cell was then shaking for 30 seconds before it was left undisturbed for another 30 seconds. One CyaniVer 4 Cyanide Reagent Powder Pillow later on is added and capped. Shake for 10 seconds and immediately add one CyaniVer 5 Cyanide Reagent Powder Pillow and recapped the sample. Delaying in the addition of the CyaniVer 5 Cyanide Reagent Powder Pillow will produce low test results. Vigorously the cells once again shake. Pink colour will develop if cyanide is present. The timer is touched and reaction will leaved to take place for 30 minutes and solution will turn from pink to blue. When the timer beeps, another cell is filled with 10 mL of sample (blank cell). The blank cell wiped then placed in the cell holder. Press zero and the display will show the amount of cyanide in mg/L. The prepared sample is wiped and placed in the cell holder. Results later on appeared in mg/L of CN. In this test, 125 gram of Potassium Cyanide and 4 liters of water and deionized water used as a standard. For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. The instrument manual need to be referred for more information on Running a Reagent Blank. Pollution Prevention and Waste Management is referred for proper disposal of solutions containing cyanide. Please refer to Figure 3.5 and 3.6 in Appendix 3-2.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 FINDINGS

Ion exchange method of Cyanide removal wastewater was found to be effective as the method successfully reduce the Cyanide content in artificial self made waste water from 1500 mg/L down to less than 5 mg/L. According to the Environmental Quality Act (EQA), maximum allowable of Cyanide content in waste water is 5 mg/L. However when some parameters or variables in the process been manipulated, the results will show different level of Cyanide content in the treated wastewater using ion exchange method.

4.2 LABORATORY EXPERIMENTS

Several variables or parameters have been selected to be manipulated during the experiments carried out in the laboratory. In this experiments five (5) possible variables have been choose to be manipulated which are Cyanide concentration, water flow rate, resin bed height, water hardness addition and total suspended solid reduction. All of the variables were observed to favor the results of the experiment accordingly.

4.2.1 Effect of Cyanide Concentration

In the first experiment, the Cyanide concentration is varied from 1500 mg/L down to 1000 mg/L and then to 500 mg/L. Those three different concentration levels of Cyanide have been run through the ion exchange unit. From the experiment three different graphs of conductivity versus time is obtained. From Figure 4.1, for cyanide concentration of 1500 mg/L; the time taken to reach breakthrough point is longer compared to Figure 4.2 and Figure 4.3. Breakthrough point for Figure 4.1 occurs after 80 seconds of elapsed time compared to 70 seconds for Figure 4.2 and 60 seconds for Figure 4.3 respectively. This showing that, with higher concentration of cyanide present in water sample the time taken for breakthrough point occurrence is longer. Beside breakthrough points, those three graph also show the different in initial conductivity. For water sample with 1500 mg/L concentration the initial conductivity is 4.0 miliSiemen (mS) while for water sample with 1000 mg/L and 500 mg/L the initial conductivity are 2.6 mS and 1.4 mS accordingly. Those three graphs also differ in minimum conductivity meter recorded i.e where the graphs maintain almost straight line before end up with straight line increasing after breakthrough point. Minimum conductivity meter for water sample of 1500 mg/L, 1000 mg/L and 500 mg/L are 1.10-1.15 mS, 0.90-0.95 mS and 0.50-0.55 mS. Both the initial and the minimum reading difference recorded were caused by the capacity of cyanide anion presence and ion exchange that occur during the process. As the concentration increase, the initial and the minimum conductivity also follow to increase or vice versa.

After treatment water sample were then test with Spectrophotometer model DR2010 for cyanide level identification. From the test, the results show that dramatic decrement of cyanide content in water sample. Water sample with 1500 mg/L cyanide reduced to 2.17 mg/L after treatment while for 1000 mg/L and 500 mg/L the equipment read 1.44 mg/L and 1.03 mg/L of cyanide content after treatment. The experiment conducted under water flowrate of 30 cm3/min. Three graphs obtained from the experiment are as below. Refer Appendix 4-1 Table 4.1 for the data collection of the experiment.

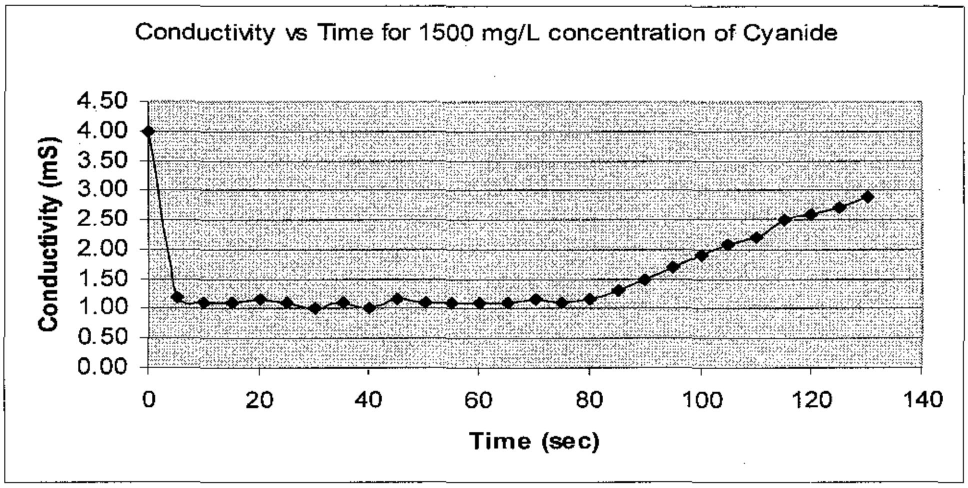


Figure 4.1: Conductivity versus Time for 1500 mg/L concentration

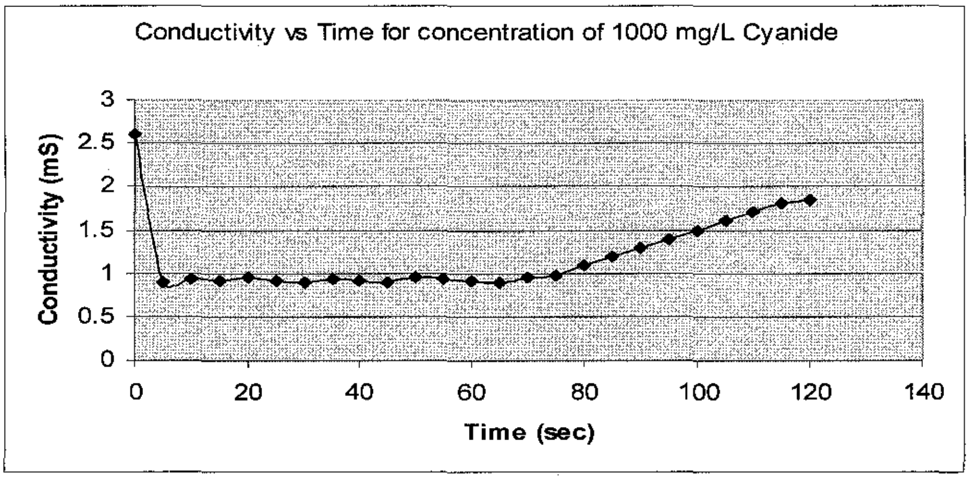


Figure 4.2: Conductivity versus Time for 1000 mg/L concentration

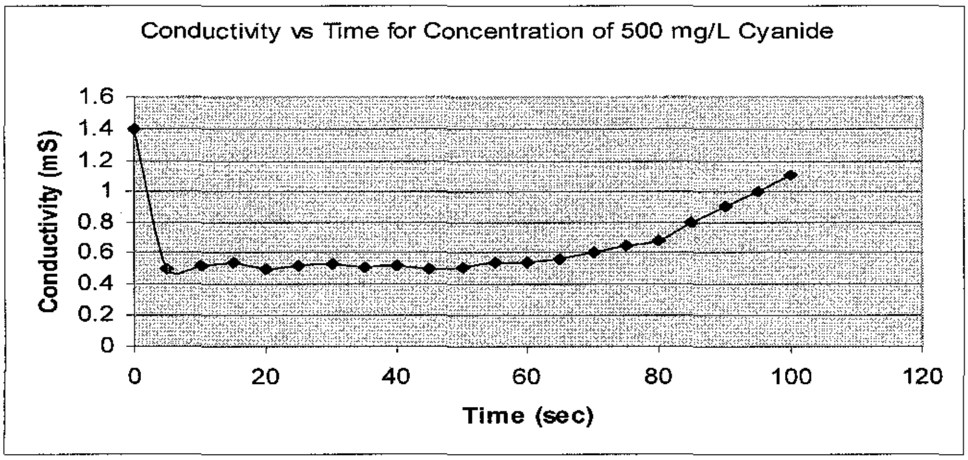


Figure 4.3 Conductivity versus Time for 500 mg/L concentration

4.2.2 Effect of Water Sample Flowrate

The ion exchange unit held in Wastewater Laboratory of UTP Chemical Engineering Department is equipped with a type-metering pump with capacity of 5 L/hr @ 10 bar delivering 50 watts power operated under electrical specification of 240VAC/1ph/50Hz that used to control the flowrate of test water running through the unit. In this experiment, manipulation of test water flowrate is conducted to observe on its effect to the results obtained. Three identified flowrate have been decided to be manipulated which are 30 cm3/min, 40 cm3/min and 50 cm3/min. The experiment was carried out under initial test water conductivity of 2.3 mS and 1000 mg/L concentration of Cyanide. At the end of the experiment three (3) graphs which are Figure 4.4, Figure 4.5 and Figure 4.6 were successfully gained. After analysis, it is found that by increasing flowrate of the test sample that run through the resin bed, the elapsed time for the process is reduced. The occurring of the breakthrough point is faster as the flowrate is increased. As the flowrate increase from 30 cm3/min to 40 cm3/min and further to 50 cm3/min the elapsed time reducing from 120 seconds to 100 seconds and last to 80 seconds. The occurrence of breakthrough points also observed to be faster which are 70 seconds for 30 cm3/min, 60 seconds for 40 cm3/min and 50 seconds for 50 cm3/min. As the flowrate is forced to go higher, the delivering of CN- amount will be greater. With greater amount of CN- embarked to the resin bed, the exhaustion time of the resin bed will be shortened which result in faster treatment of a test water. However, bigger amount of CN- pass through the resin bed rapidly, the resin would not be able to absorb the CN- accordingly. This will results in higher CN- content in the treated test water. The DR2010 read the value of 1.64 mg/L of CN- present in treated test water with 40 cm3/min flowrate, while 1.85 mg/L CN- detected in treated test water with 50 cm3/min compared to only 1.44 mg/L CN- with 30 cm3/min flowrate. Increasing in flowrate might help quantitatively and saving time but not to the qualitative point of view. The graphs obtained would show clearer view on the effect of flowrate to the process operation. Refer to Appendix 4-1 Table 4.2 for the data collection during the experiment.

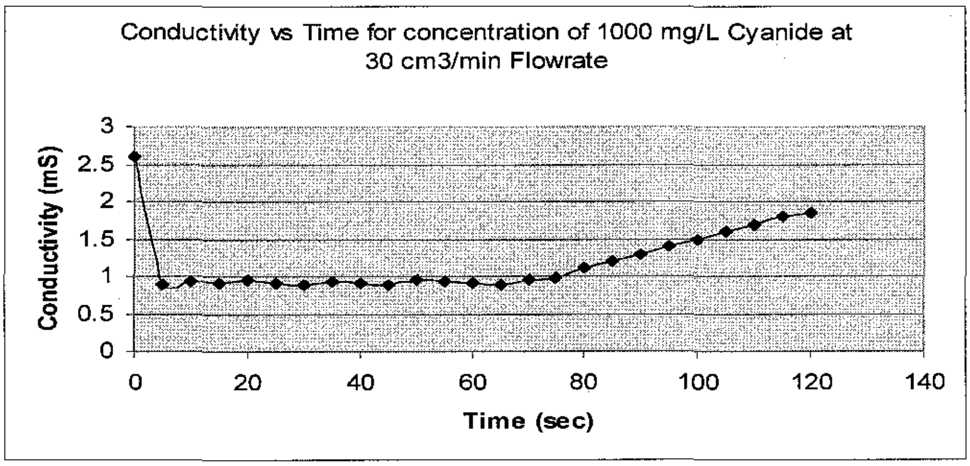


Figure 4.4: Conductivity versus Time at 30 cm3/min flowrate

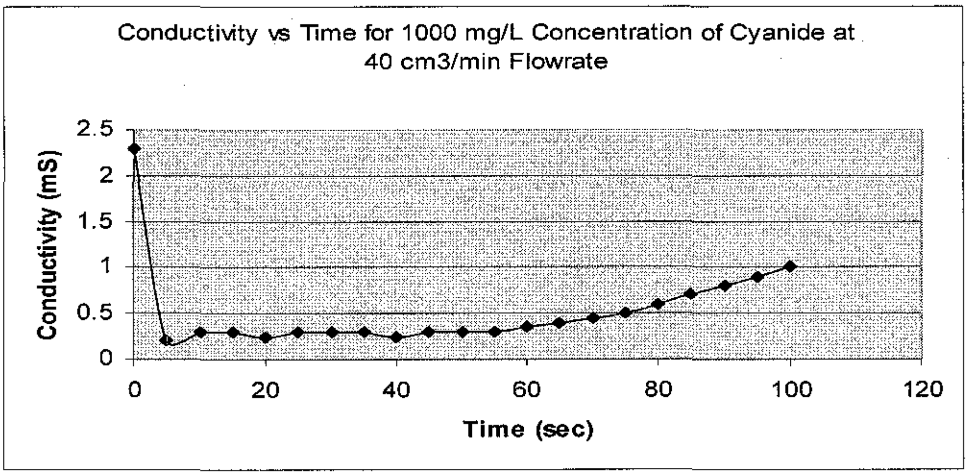


Figure 4.5: Conductivity versus Time at 40 cm3/min flowrate

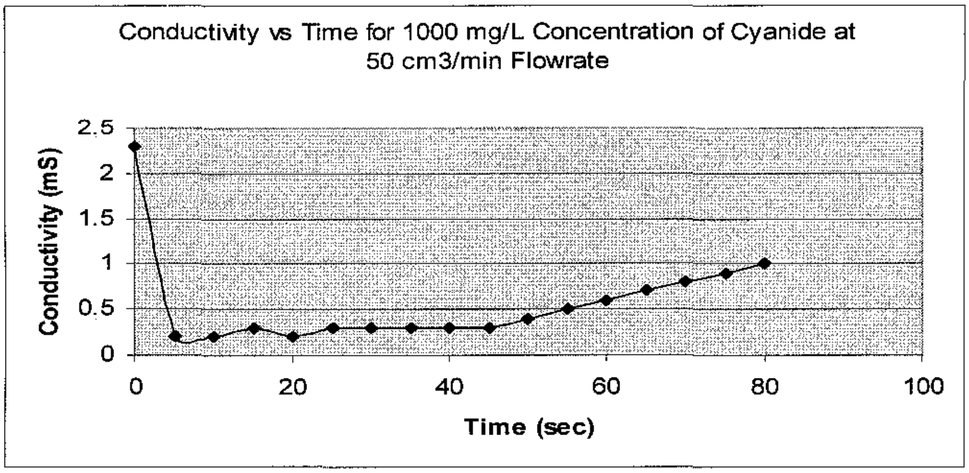


Figure 4.6: Conductivity versus Time at 50 cm3/min flowrate

4.2.3 Effect of Resin Bed Height

Resin bed regularly used for the ion exchange unit is at 52 cm height placed in 20mm diameter column. The height of the column presumes the capacity of the resin bed to exchange ion with the test water. As the bed height increase the capacity of the resin is also increased or vice versa. In this part of experiment, the height of the resin bed is varied from 52 cm height, 40 cm height and lastly to 30 cm height. The test water used in this experiment is the same as the flowrate experiment which is 1000 mg/L of cyanide in concentration. The flowrate of the test water is kept at 30 cm3/min. The results of this part of experiment comprises of three (3) identical graphs which are Figure 4.7, Figure 4.8 and Figure 4.9 each for 52 cm, 40 cm and 30 cm height of resin. The highest resin bed (52cm) elapsed 120 seconds to finish the experiment where the breakthrough occurs at seventieth (70) seconds, the middle (40 cm) elapsed 90 seconds length of experiment with the occurrence of breakthrough point at fifty fifth (55) seconds while for the lowest resin bed (30 cm) the elapsed time is only 70 seconds with the breakthrough point at thirty fifth (35) seconds. The graphs plotted indicate the differences. Refer to Appendix 4-1 Table 4.3 for the data collection during the experiment.

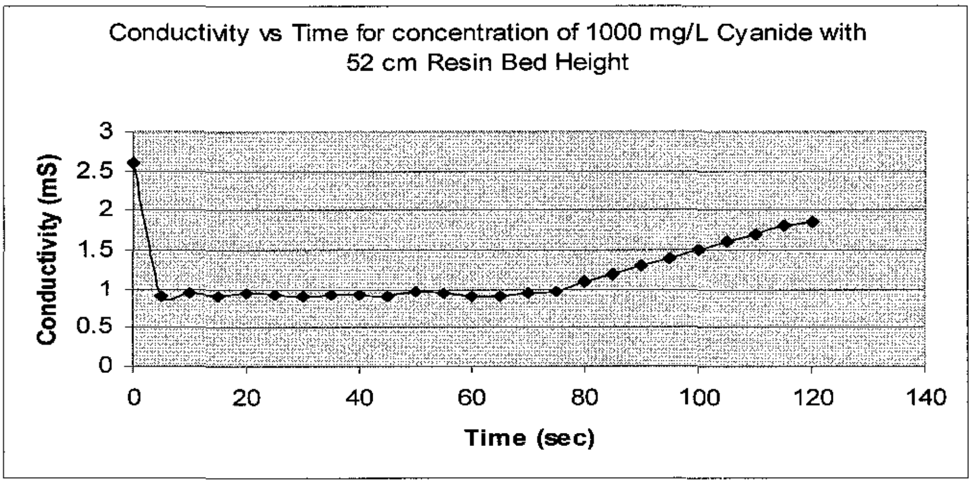


Figure 4.7: Conductivity versus Time with 52 cm Bed Height

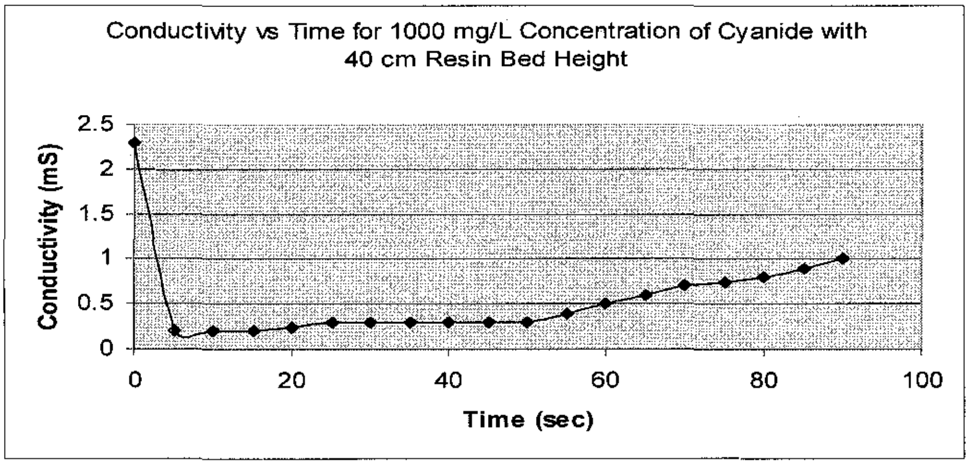


Figure 4.8: Conductivity versus Time with 40 cm Bed Height

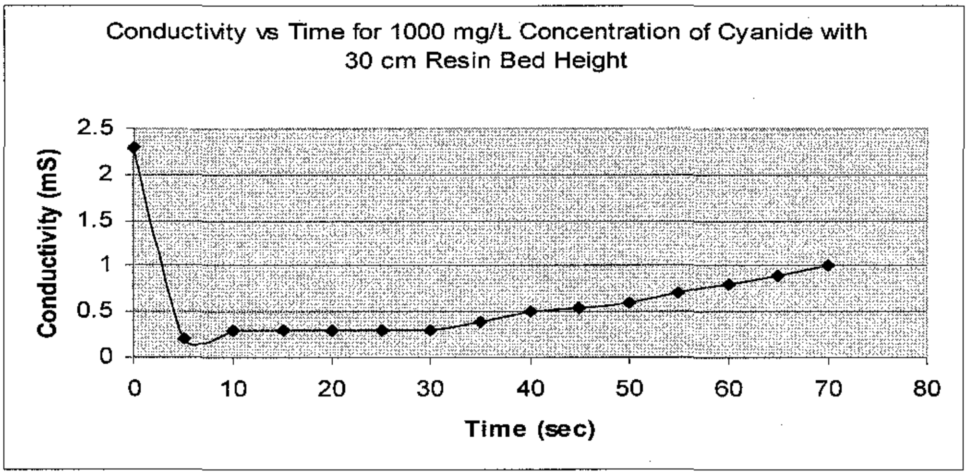


Figure 4.9: Conductivity versus Time with 30 cm Bed Height

4.2.4 Effect of Additional Water Hardness

Additional water hardness to the test water was another manipulated variable that the fourth part of the experiment dealt with. In this part, Calcium Carbonate (CaCO3) was selected to be added to the artificial wastewater to investigate on the effect of its addition to the ion exchange process operation. In this part, the additional of CaCO3 was done in to the test water in three (3) separate steps with three (3) different amount which are 150 mg/L, 300 mg/L and 450 mg/L. The initial test water was prepared with concentration of

1000 mg/L and run through 52 cm bed height with 30 cm3/min flowrate. The outcome of the experiment was achieved where three (3) graphs which are Figure 4.10, Figure 4.11 and Figure 4.12 were successfully develop one for each amount of CaCO3 addition to the test sample. From the analysis, the bigger amount of CaCO3 added to the test sample, the shorter the elapsed time for the process gained. The elapsed time for each experiment decreases from 110 seconds to 80 seconds and further to 60 seconds as the increases of CaCO3 amount added which are 150 mg/L, 300 mg/L and 450 mg/L. The behaviour of the graphs and elapsed time due to the additional ion present in the test water i.e Ca^{2+} and CO_3^{-2}. This will cause selectivity problems to the polymer resin as some other type of ions presented which affected the amount of the desired CN- to be removed. Decreasing of the elapsed time at the same time shortened the time for bed exhaustion or saturation. This is due to the excess amount of ions present with fixed height of the resin bed height. So it reach saturation point earlier compared to the process that involving no water hardness as previous experiment.

Moreover, the results obtained from HACH wastewater analysis also showing higher amount of cyanide content in the treated test water. The untreated CN- is due to the present of the additional ions especially CO_32- which compete with CN- to be absorbed by the polymer resin. The resin selectivity decreases upon CN- is no longer reaches its optimum point when additional ions managed to be presented in the test water. The amount of CN- obtained from DR2010 are 3.72 mg/L, 4.24 mg/L and 4.89 mg/L each for 150 mg/L, 300 mg/L and 450 mg/L of $CaCO_3$ addition to the test water. The untreated CN- almost double compared to what is obtained from the treated test water without $CaCO_3$ present in them. The data obtained were then converted into graphs as below. Refer to Appendix 4-1 Table 4.4 for the data collection of the experiment.

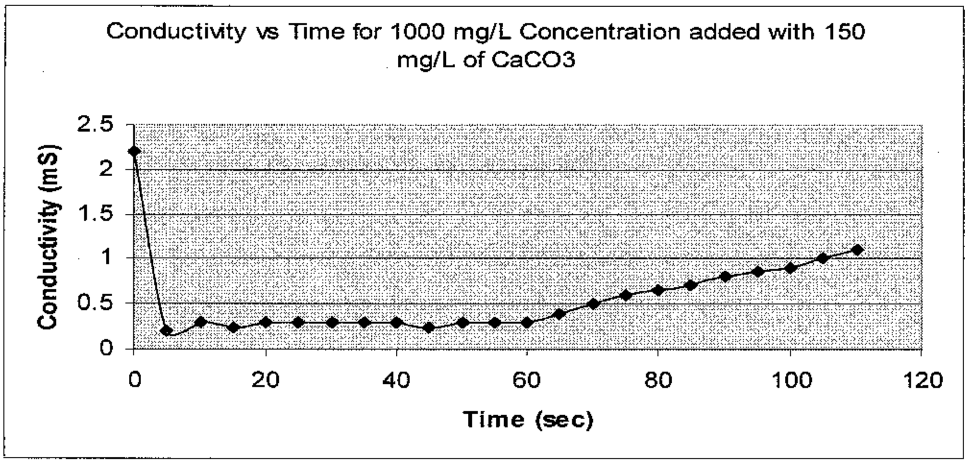


Figure 4.10: Conductivity versus Time with 150 mg/L $CaCO_3$

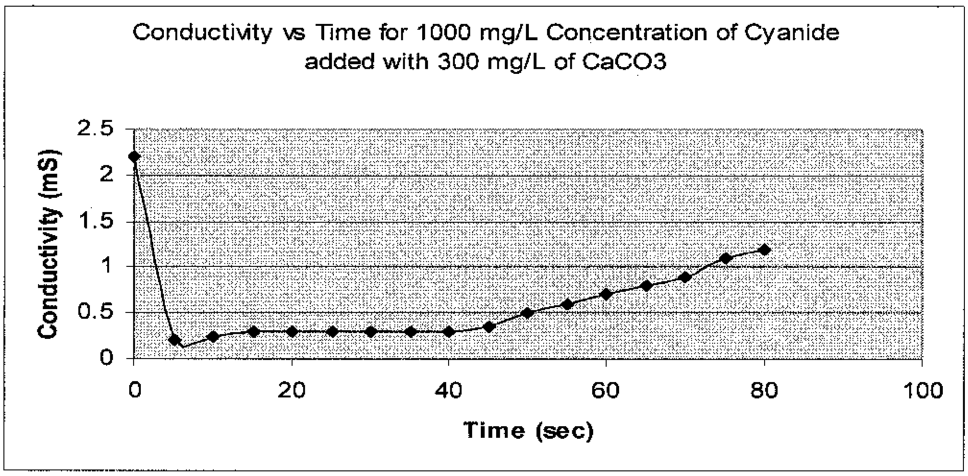


Figure 4.11: Conductivity versus Time with 300 mg/L $CaCO_3$

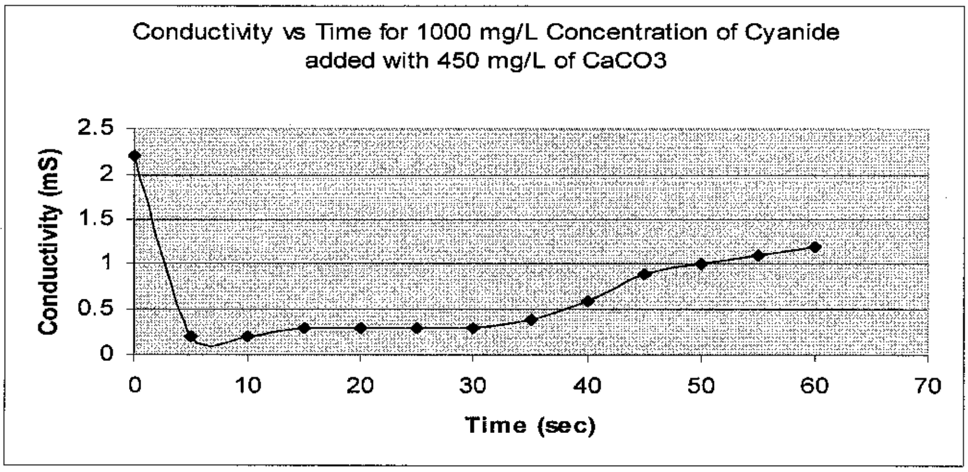


Figure 4.12: Conductivity versus Time with 450 mg/L $CaCO_3$

4.2.5 Effect of Suspended and Colloidal Impurities.

In this part of experiment, the test water initially undergoes coagulation and flocculation process where the process consolidates suspended and colloidal impurities. Aluminium sulphate, $Al_2(SO_4)_3$ or commonly know as alum is used as a coagulant. The function of coagulant is to destabilize the colloids and help then agglomerate to attain desired settling characteristic. The more coagulant added to the sample water, the more suspended and colloidal impurities could be extracted from the test water. For this experiment, comparison between the test water which not undergo coagulation and flocculation process with the one that undergo it with different amount of coagulant added to the test water. Two (2) separate experiments have been carried out each with 10g of alum and 20g of alum added to the test water before went through coagulation and flocculation process. Increasing amount of alum to the test sample will increase the amount of consolidates suspended collected at the bottom of the beaker leaving the test sample looking clearer compared with the one before the process. The treated test water under this process was then run through ion exchange unit. Two (2) graphs obtained and it then compared to the one which was not treated using the coagulation and flocculation process. The graphs comparison as below:

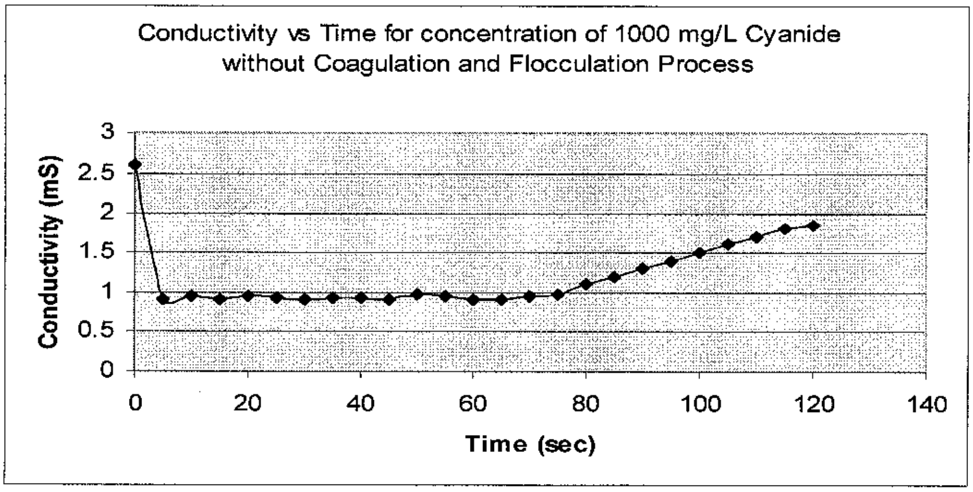


Figure 4.13: Conductivity versus Time without Coagulation and Flocculation Process

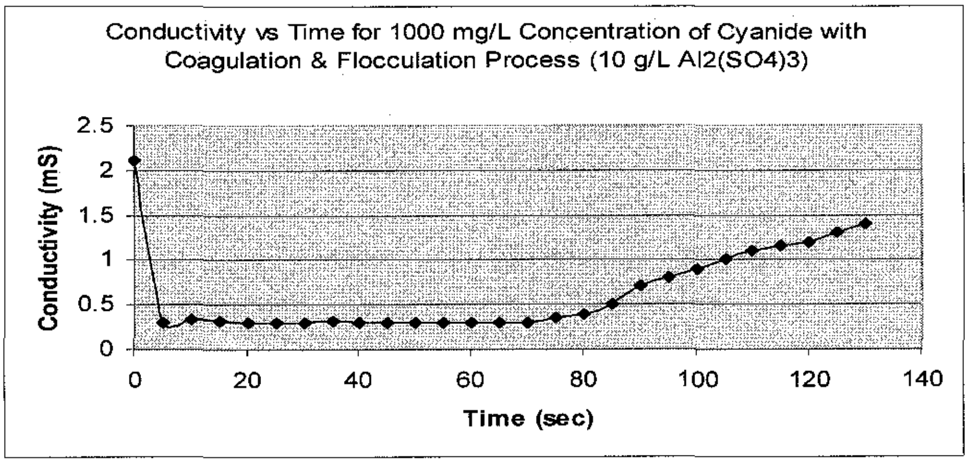


Figure 4.14: Conductivity versus Time with 10g alum (coagulant)

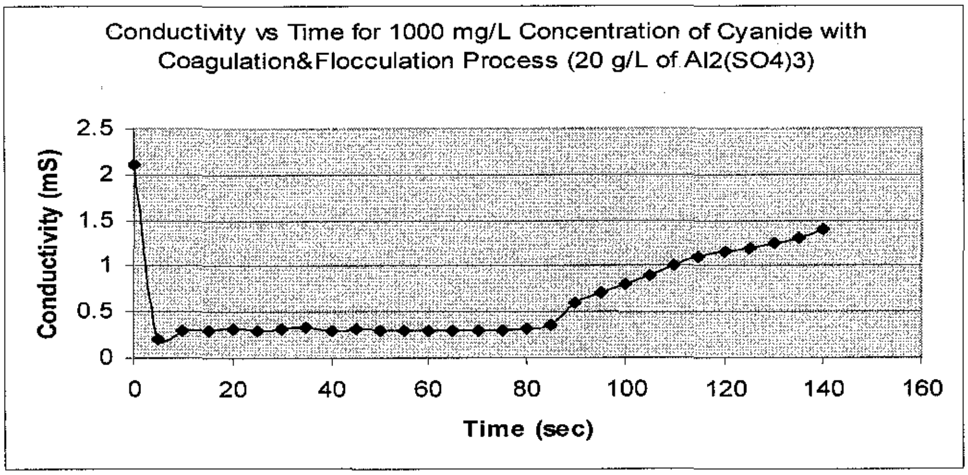


Figure 4.15: Conductivity versus Time with 20g alum(coagulant)

From the graphs, the elapsed times for those three (3) graphs are different. The elapsed time is determined by the occurrence of the breakthrough point or saturation point for the polymer resin. The more coagulant that we add to the test water will result to the longer elapsed time gain by the process. As the coagulant added increase during coagulation and flocculation process, the consolidation of suspended and colloids impurities increase. Thus leaving the treated test water sample freer from the effluents. When the treated test water run through ion exchange unit, it elapsed greater time due to less suspended or impurities that plug the surface area of the polymer resin. The lesser the suspended in the water, the longer polymer resin would withstand before its saturation point as well as better absorption of desired ions (CN-). HACH DR2010 reads

1.24 mg/L and 1.03 mg/L for each 10g and 20g additional of alum to the test water. Refer to Appendix 4-1 on Table 4.5 for the data collection of the experiment.

4.3 PROBLEMS FACED AND RECOMMENDATIONS

4.3.1 Problems Faced

4.3.1.1 Early of the Project Study

In the early stage of the project, the intended project requirement is to remove Boron from wastewater using ion exchange. However, the procedure failed to make Boron arrived on site within the time frame. The disappointment with regards to the Boron availability problems was not been highlighted earlier. The problem was addressed by the respective group of people to the owner of the project in the middle of the semester after all information and literature research was properly done. As a matter of fact, the 7 weeks back of study period has been wasted. For the sake of project continuation, project owner was advised to change the chemical from Boron to Cyanide. Literature review and information gathering was again restart for the new chemical. Putting great effort onto the new project title was only a way to make the project realized. Fortunately, the project was successfully done within the left of the study period.

Resin availability is another problem where only two (2) types resin available at site. One is strong acid resin which appropriate for decationization process and another one is neutral resin. However, cyanide removal requires deanionizaton process which must the best resin to be assembled was strong base type of resin. Within the time frame left, it is impossible for the resin to be on site on the date and time estimated. Thus the neutral resin available was looked to be the best for this study.

4.3.1.2 Cyanide Test

Cyanide was well known as a very hazardous chemical and need for proper procedure of handling. For the project justification, the treated test water sample need to be analyzed to investigate on the remaining CN- left. Some method has been justified for the analysis for example Atomic Absorption Spectroscopy (AAS), Gas Chromatography/Mass Spectroscopy (GCMS), High Performance Liquid Chromatography (HPLC), complex titration method and lastly HACH kit waste water analysis method. All of the equipment stated above is available on site but, the test could not be conducted due to unavailable standard for the test. For the sake of the experiment, the test was suggested to be outsourced for the analysis. Jabatan Penyelidikan Galian dan Bahan in Ipoh has been conducted for the test. The department used to do cyanide test before but it was no longer practiced since the complexing agent for cyanide which is barbiturate acid was banned by the Department of Environment (DOE). The unavailability for the cyanide test has lead to the last alternative which is by using HACH kit waste water analysis.

4.3.1.3 HACH kit wastewater analysis

HACH kit wastewater analysis has its limitation. The main limitation was the amount that could be detected by the equipment (DR/2010) is only up to 0.240 mg/L of CN-. The treated test water is expected to be left with greater amount than the DR2010 could detect. However, the device still applicable for the analysis if the test water is diluted over and over until the device is capable to detect the level of CN-. Using this one and only available method did delaying the time for the analysis. As the dilution is not enough, another analysis should be done. The interval reaction time for the reagent to detect the present of CN- last for 30 minutes for a set of analysis. If the test water sample was not enough diluted, the reader of the device could not be able to read the value as it is over the range. Thus for new sample analysis, another 30 minutes reaction will take place. Those AAS, HPLC and GCMS will give the result analysis faster than the HACH DR/2010 that the analysis dealt with.

4.3.2 Recommendations

4.3.2.1 Project Management and Coordination

First of all, it is suggested that any project given to the student should be ensured of the flexibility of the infrastructures that related to the project. Meaning to say, when the project is given for a particular person to study the entire expected requirement should be considered within the reachable scope. The availability of the equipments, software, apparatus and guidance will help the researcher a lot in producing a good paper. Difficulties in getting the tools and equipment will demoralize the researcher although the project is very interesting. Lack of communication and accountability should be avoided for better managerial, technical and capability building as guided in PETRONAS triple plus policy. With good communication, devices and tools availability and effort from the researcher, a good project will be produced even the best one could achieved. Close supervision is suggested but it is not compulsory as this is so call an independent project for the researcher before going to the real world of industries and research.

4.3.2.2 Project Improvement

This study for cyanide removal using ion exchange still has a window of improvement. There are many aspects and point view that has not been studied for example extra good resin that should be used, different type of test water and also the better method of CN- quantitative test. Besides those identified criteria of improvement, there might be other point of view that the researcher has missed looked. Some other researcher could have think in different way and looking forward to detail out the study better than what has been presented in this paper. All those kind of efforts are highly welcomed to improve as well as enhance the study that has been reported in the paper. This paper could be looked as a single step for a long journey with regards to the topic in research and development field for the benefit of human beings.

CHAPTER 5

CONCLUSION

The study on removal of cyanide from wastewater has fulfilled the objectives performed in beginning of the project. From the experiments and test that have been conducted through out the study period, it could be concluded that the ion exchange method is proven effective for cyanide removal from waste water. However, the effectives increase and decrease with regards to the variables manipulated within the experiments conducted which are concentration of cyanide, test water flowrate, resin bed height, additional of water hardness ($CaCO_3$) and suspended and colloidal impurities. As the concentration of cyanide in test water is lowered, the breakthrough point occurrence was observed to be faster or vice versa. When the test water flowrate is increased in the experiment, the time taken for separation process is reduced. However the cyanide concentration left after treatment was found to be greater compared to normal flowrate applied. Heights of the resin bed also play a role in determining the effectiveness of the process. When the resin bed height reduced the time taken for breakthrough occurrence followed to reduce. By reducing the bed height the effectiveness of ion exchange method decreasing and vice versa. Water hardness content also affects the effectiveness of this method. From the experiment, as the amount of $CaCO_3$ added to test water increase the breakthrough point was observed to appear faster. Meaning, the amount of water hardness inversely proportional to the effectiveness of cyanide removal. The last variable manipulated in the experiment which is suspended and colloidal impurities also showing an inverse proportionality with regards to the effectiveness of cyanide removal. The increment in suspended and colloidal impurities will exhaust the resin bed earlier thus cause the more amount of cyanide pass through untreated.

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www.rohmhaas.com
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www.eco-usa.net

APPENDICES

APPENDIX 3-1

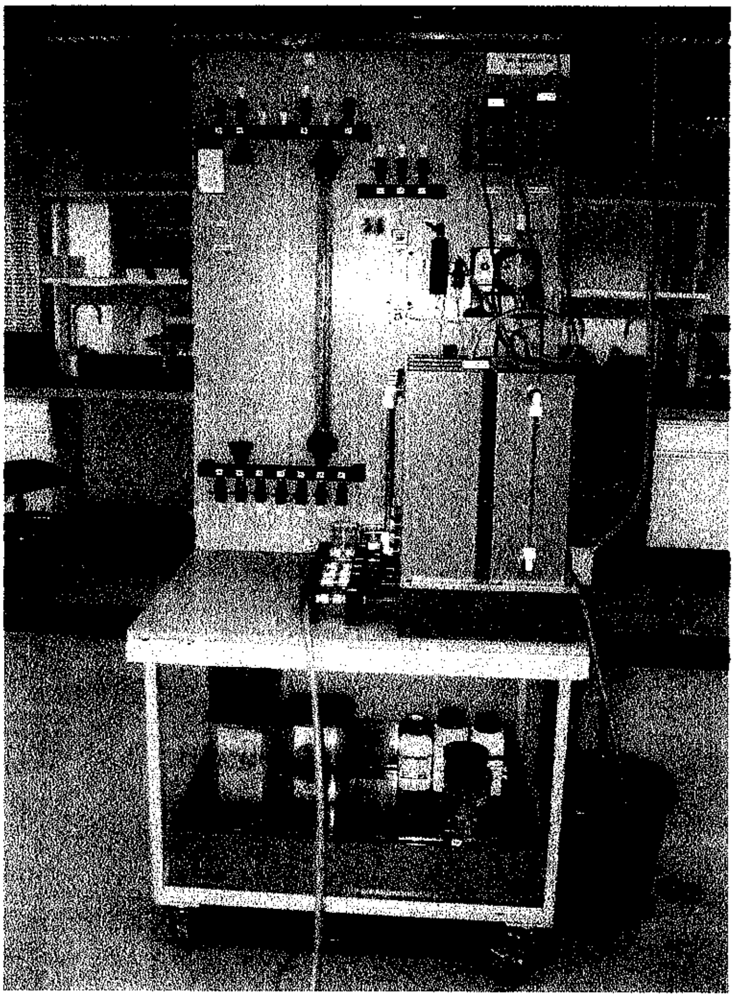


Figure 3.1: SOLTEQ ion exchange unit in WWT laboratory

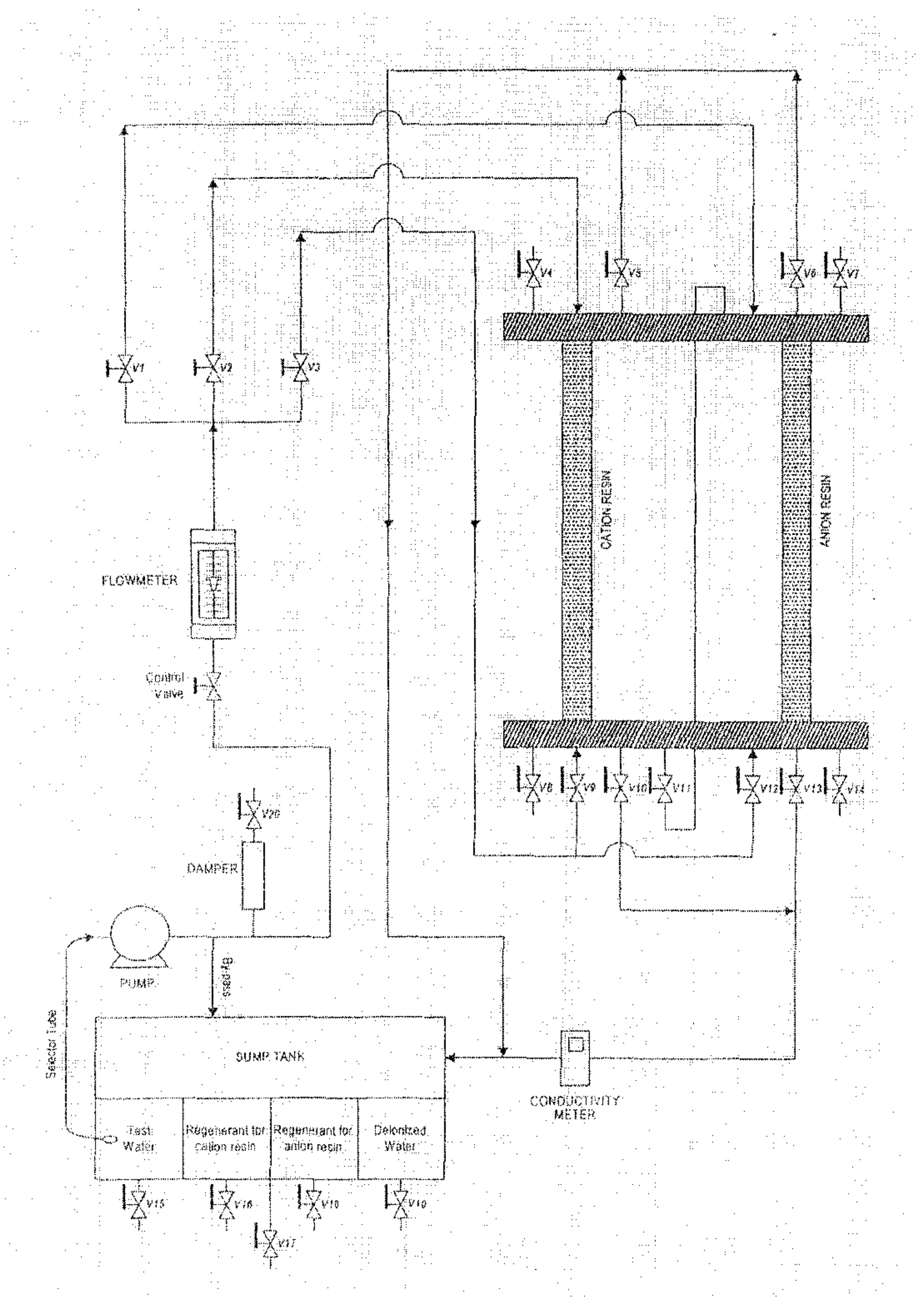
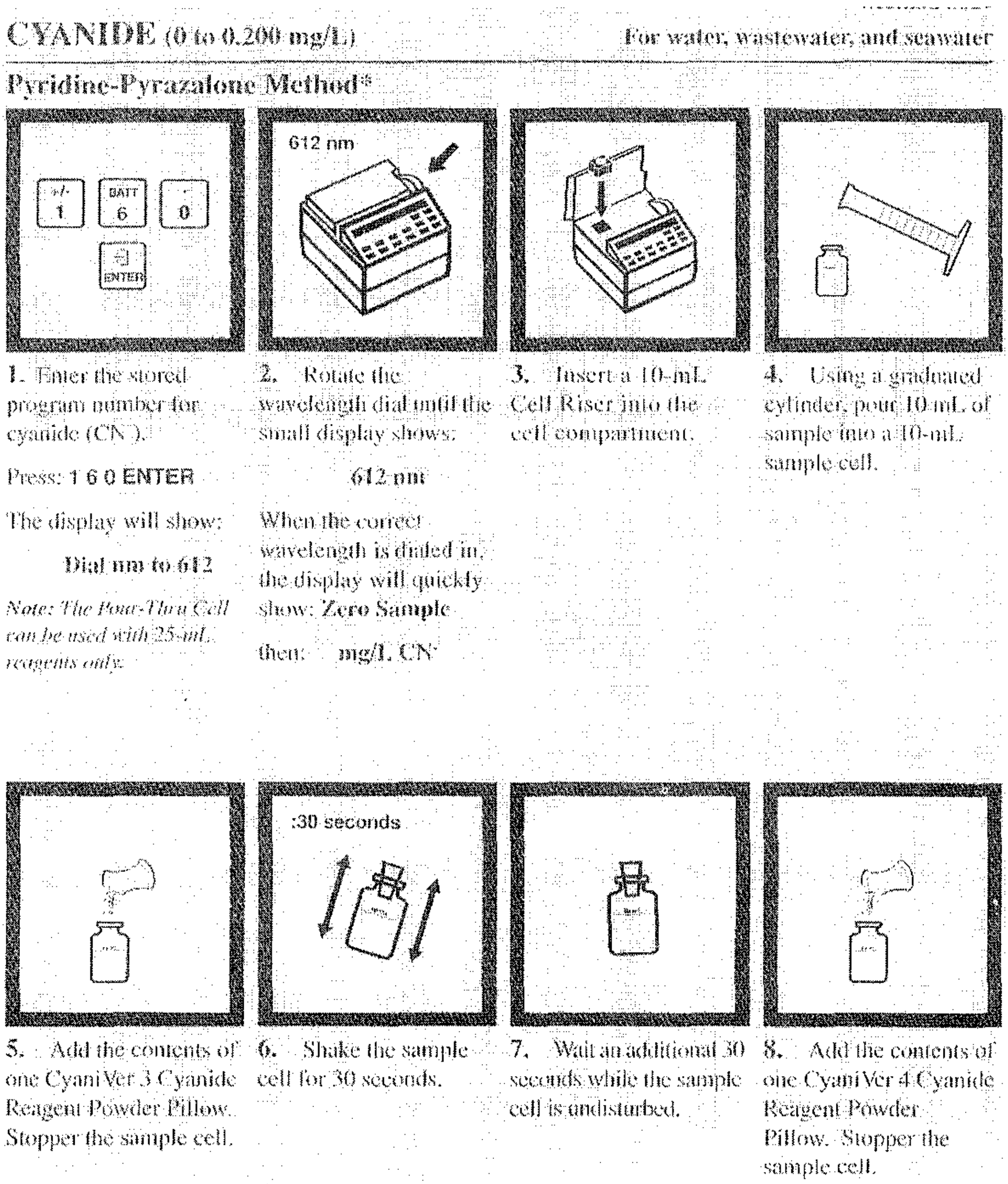


Figure 3.2: Process Flow Diagram of SOLTEQ ion exchange unit

APPENDIX 3-2

Figure 3.3: LEWATIT C240 used in the experiment

APPENDIX 3-3



CYANIDE (0 to 0.200 mg/L) For water, wastewater, and seawater

Pyridine-Pyrazalone Method*

1. Enter the stored program number for cyanide (CN^-).

Press: 1 6 0 ENTER

The display will show:

Dial nm to 612

Note: The Pour-Thru Cell can be used with 25-mL reagents only.

2. Rotate the wavelength dial until the small display shows:

612 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L CN^-**

3. Insert a 10-mL Cell Riser into the cell compartment.

4. Using a graduated cylinder, pour 10 mL of sample into a 10-mL sample cell.

5. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow. Stopper the sample cell.

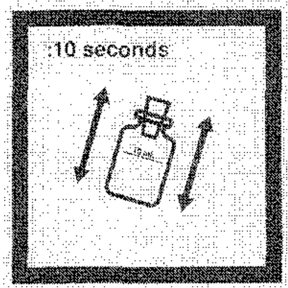
6. Shake the sample cell for 30 seconds.

7. Wait an additional 30 seconds while the sample cell is undisturbed.

8. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow. Stopper the sample cell.

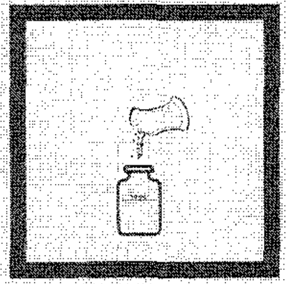
Figure 3.4: Procedure for HACH Spectrophotometer DR/2010 analysis

CYANIDE, continued



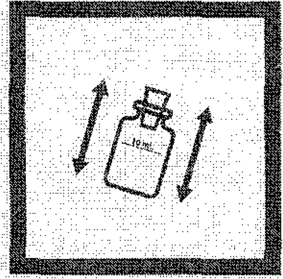
9. Shake the sample cell for ten seconds. Immediately proceed with Step 10.

Note: Accuracy is not affected by undissolved CyaniVer 4 Cyanide Reagent Powder.



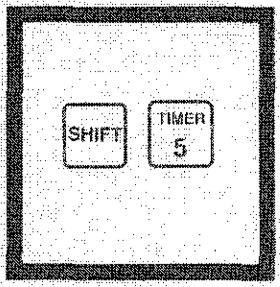
10. Add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow. Stopper the cell.

Note: Delaying the addition of the CyaniVer 5 Cyanide Reagent Powder for more than 30 seconds after the addition of the CyaniVer 4 Cyanide Reagent Powder will give lower test results.



11. Shake vigorously to completely dissolve the CyaniVer 5 Cyanide Reagent Powder (the prepared sample).

Note: If cyanide is present, a pink color will develop which then turns blue after a few minutes.

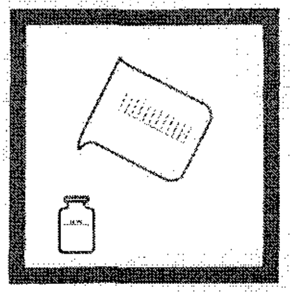


12. Press:

SHIFT TIMER

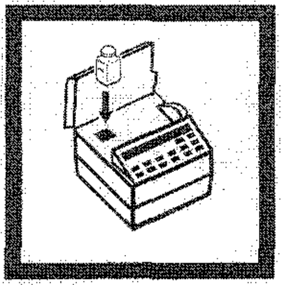
A 30-minute reaction period will begin.

Note: Samples at less than 25 °C require longer reaction time and samples at greater than 25 °C give low test results.

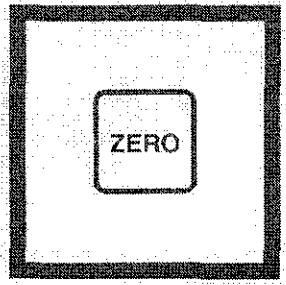


13. When the timer beeps, the display will show: **mg/L CN^-**

Fill another 10-mL sample cell (the blank) with 10 mL of sample.



14. Place the blank into the cell holder. Close the light shield.

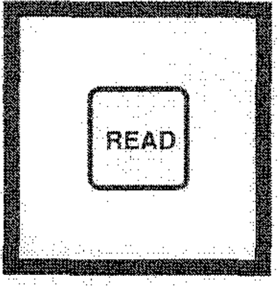


15. Press: **ZERO**

The display will show:

Zeroing...

then: **0.000 mg/L CN^-**



16. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading...

then the result in mg/L cyanide will be displayed.

Figure 3.4: Procedure for HACH Spectrophotometer DR/2010 analysis (continued)

Figure 3.5: DR/2010 HACH Spectrophotometer DR/2010

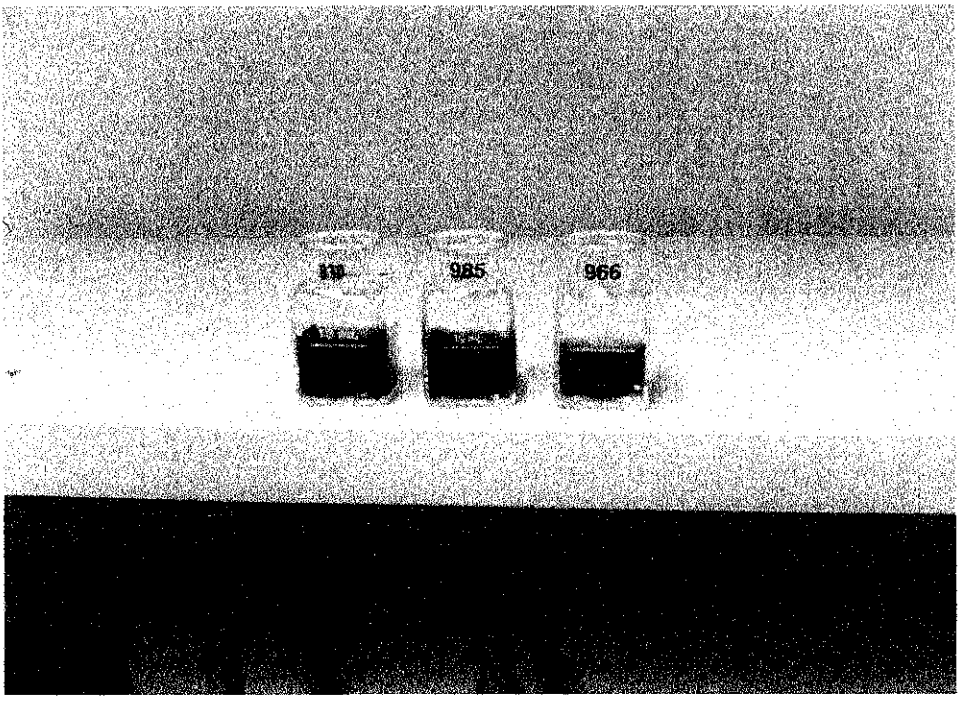


Figure 3.6: Sample for Cyanide test by Spectrophotometer DR/2010

APPENDIX 4-1

1500 mg/L		1000 mg/L		500 mg/L	
Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)
0	4.00	0	2.60	0	1.40
5	1.20	5	0.90	5	0.50
10	1.10	10	0.94	10	0.52
15	1.10	15	0.91	15	0.54
20	1.15	20	0.95	20	0.50
25	1.10	25	0.92	25	0.52
30	1.00	30	0.90	30	0.53
35	1.10	35	0.93	35	0.51
40	1.00	40	0.92	40	0.52
45	1.15	45	0.90	45	0.50
50	1.10	50	0.96	50	0.51
55	1.10	55	0.94	55	0.54
60	1.10	60	0.91	60	0.54
65	1.10	65	0.90	65	0.56
70	1.15	70	0.95	70	0.60
75	1.10	75	0.98	75	0.65
80	1.15	80	1.10	80	0.68
85	1.30	85	1.20	85	0.80
90	1.50	90	1.30	90	0.90
95	1.70	95	1.40	95	1.00
100	1.90	100	1.50	100	1.10
105	2.10	105	1.60		
110	2.20	110	1.70		
115	2.50	115	1.80		
120	2.60	120	1.85		
125	2.70				
130	2.90				

Table 4.1: Table of Conductivity and Time for Concentration Experiment

APPENDIX 4-1

30 cm3/min		40 cm3/min		50 cm3/min	
Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)
0	2.60	0	2.30	0	2.30
5	0.90	5	0.20	5	0.20
10	0.94	10	0.30	10	0.20
15	0.91	15	0.30	15	0.30
20	0.95	20	0.25	20	0.20
25	0.92	25	0.30	25	0.30
30	0.90	30	0.30	30	0.30
35	0.93	35	0.30	35	0.30
40	0.92	40	0.25	40	0.30
45	0.90	45	0.30	45	0.30
50	0.96	50	0.30	50	0.40
55	0.94	55	0.30	55	0.50
60	0.91	60	0.35	60	0.60
65	0.90	65	0.40	65	0.70
70	0.95	70	0.45	70	0.80
75	0.98	75	0.50	75	0.90
80	1.10	80	0.60	80	1.00
85	1.20	85	0.70		
90	1.30	90	0.80		
95	1.40	95	0.90		
100	1.50	100	1.00		
105	1.60				
110	1.70				
115	1.80				
120	1.85				

Table 4.2: Table of Conductivity and Time for Flowrate Change Experiment

APPENDIX 4-1

52 cm		40 cm		30 cm	
Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)
0	2.60	0	2.30	0	2.30
5	0.90	5	0.20	5	0.20
10	0.94	10	0.20	10	0.30
15	0.91	15	0.20	15	0.30
20	0.95	20	0.25	20	0.30
25	0.92	25	0.30	25	0.30
30	0.90	30	0.30	30	0.30
35	0.93	35	0.30	35	0.40
40	0.92	40	0.30	40	0.50
45	0.90	45	0.30	45	0.55
50	0.96	50	0.30	50	0.60
55	0.94	55	0.40	55	0.70
60	0.91	60	0.50	60	0.80
65	0.90	65	0.60	65	0.90
70	0.95	70	0.70	70	1.00
75	0.98	75	0.75		
80	1.10	80	0.80		
85	1.20	85	0.90		
90	1.30	90	1.00		
95	1.40				
100	1.50				
105	1.60				
110	1.70				
115	1.80				
120	1.85				

Table 4.3: Table of Conductivity and Time for Bed Height Experiment

APPENDIX 4-1

150 mg/L $CaCO_3$		**300 mg/L $CaCO_3$**		**450 mg/L $CaCO_3$**	
Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)
0	2.20	0	2.20	0	2.20
5	0.20	5	0.20	5	0.20
10	0.30	10	0.25	10	0.20
15	0.25	15	0.30	15	0.30
20	0.30	20	0.30	20	0.30
25	0.30	25	0.30	25	0.30
30	0.30	30	0.30	30	0.30
35	0.30	35	0.30	35	0.40
40	0.30	40	0.30	40	0.60
45	0.25	45	0.35	45	0.90
50	0.30	50	0.50	50	1.00
55	0.30	55	0.60	55	1.10
60	0.30	60	0.70	60	1.20
65	0.40	65	0.80		
70	0.50	70	0.90		
75	0.60	75	1.10		
80	0.65	80	1.20		
85	0.70				
90	0.80				
95	0.85				
100	0.90				
105	1.00				
110	1.10				

Table 4.4: Table of Conductivity and Time for Additional Water Hardness

APPENDIX 4-1

No Alum		10g Alum		20g Alum	
Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)	Time (sec)	Conductivity (mS)
0	2.10	0	2.10	0	2.60
5	0.20	5	0.30	5	0.90
10	0.30	10	0.33	10	0.94
15	0.30	15	0.31	15	0.91
20	0.32	20	0.30	20	0.95
25	0.30	25	0.30	25	0.92
30	0.32	30	0.30	30	0.90
35	0.33	35	0.31	35	0.93
40	0.30	40	0.30	40	0.92
45	0.31	45	0.30	45	0.90
50	0.30	50	0.30	50	0.96
55	0.30	55	0.29	55	0.94
60	0.30	60	0.30	60	0.91
65	0.30	65	0.30	65	0.90
70	0.30	70	0.30	70	0.95
75	0.30	75	0.35	75	0.98
80	0.31	80	0.40	80	1.10
85	0.35	85	0.50	85	1.20
90	0.60	90	0.70	90	1.30
95	0.70	95	0.80	95	1.40
100	0.80	100	0.90	100	1.50
105	0.90	105	1.00	105	1.60
110	1.00	110	1.10	110	1.70
115	1.10	115	1.15	115	1.80
120	1.15	120	1.20	120	1.85
125	1.20	125	1.30		
130	1.25	130	1.40		
135	1.30				
140	1.40				

Table 4.5: Table of Conductivity and Time for Suspended and Colloidal Impurities