A Final Dissertation

# Reuse of Water-Treatment-Plant Sludge Coagulants for Water and Wastewater Treatment

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CERTIFICATION OF APPROVAL

**Reuse of Water-Treatment-Plant Sludge Coagulants for Reusing in Water and Wastewater Treatment**

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## ABSTRACT

This study focused to investigate the effectiveness of recycled iron sludge (RIS) coagulants for reuse in treating various wastewater streams. Leachate from Kelantan landfill, river water and petroleum refinery waste were being used in for this study to evaluate the effectiveness of the recycled iron sludge (RIS). Parameters such as pH, turbidity, and chemical oxygen demand (COD) were evaluated. For leachate treatment, RIS coagulant is comparable to alum to treat leachate, with a slight removal of COD at 36% for alum and 8% for RIS. However, it is crucial to evaluate the pH since this metal coagulant is acidic and the coagulant addition may consume alkalinity and results in very acidic treated samples. Addition of 1 mL of RIS coagulant into water sample removed the turbidity to 95%. When the dosage was further increased to 60 mL, the removal increased slightly to 97%. It is also found that the optimal dosage of RIS for petroleum refinery wastewater treatment was 114.74 mg/L, with the final pH of 10.8. The second phase of the project was focused on only petroleum refinery waste where a series of jar test was conducted to obtain the optimum dosage pH for alum and RIS, which were found to be 9 and 10 respectively. Without adjusting the pH, the petroleum refinery waste treatment using RIS as a coagulant showed that 20 mg/L of RIS removed 95% of COD. The test was repeated with pH adjustment to 10, and it is showed 120 mg/L were needed to remove 97% of COD with the final pH of 7.6.

**ACKNOWLEDGMENT**

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Coagulation is a process of adding a chemical coagulant or coagulants to destabilize the colloidal particles so that particle growth can occur as a result of particle collision. For the coagulation process, jar tests are conducted to determine the optimum dosage of coagulants used. Besides commercial coagulant such as alum ($Al_2(SO4)_3$), ferric chloride ($FeCl_3$) and organic polyelectrolytes, recovered or natural coagulant has long been used throughout the industry. These metal salts are for particulates and some complex dissolved contaminants and they result in significant savings in minimizing the expenditure on commercial coagulants [1].

The first phase of the project is to evaluate the effectiveness of the recycled iron sludge (RIS) coagulant compared to alum ($Al_2(SO4)_3$) and ferric chloride ($FeCl_3$). Alum and ferric chloride are used in the project due to their ease of availability in local market and their better performance in removing suspended solids. Leachate from a landfill in Kelantan was used as the water sample to be treated. The dosing rates of the coagulants depend on the characteristics of the waste water treated and determined from laboratory experiments. Then, the second phase of the project used the RIS coagulant for turbidity removal of surface water and treatment of petroleum refinery waste. Parameters such as pH, chemical oxygen demand (COD), turbidity and efficiency in metal removal were measured in determining the optimum pH and dosage for the coagulant.

## 1.2 Problem Statement

Water treatment industry is facing a common problem of sludge disposal. This is because whatever operations or processed used for the treatment of waste water, sludge remain as the largest in volume compared to the other constituents removed during the treatment process [2]. Disposing the solids or sludge removed during the treatment process by returning them to the surface water will cause possible side effects to the environment. Nevertheless, treatment of sludge is costly that most water treatment plants are left with no other option than disposing it. The problem of dealing with sludge is complex because only a small portion of the sludge is solid matter and the rest is a liquid, which should be treated first before it is dumped in water bodies or land. At the moment, reclamation and recycling are seen as the most economically effective solutions to this problem which encourages pollution prevention through methods such as source reduction and waste recycling [3].

Other than that, volume reduction, coagulation and settling velocity of sludge are affected by pH. The efficiency of coagulant recovery and solid reduction depended on the pHs. Adjusting the pH during the jar test during rapid mixing may be the best option to get the effective pH range for the coagulant such as ferric chloride and alum [4].

### 1.3 Objectives and Scope of Study

This project studied the effectiveness of the recycled iron sludge (RIS) coagulant and compared it with typical commercial coagulant such as alum and ferric chloride. The optimum pH and optimum chemical dosage of the coagulants were determined by using the jar tests. The project also aims to minimize the expenditures on typical commercial coagulants by maximizing the recovery and reuse of iron salts contained in the sludge, thus comparing it to other available commercial coagulant, such as Alum in terms of optimum dosage and pH, and also removal of turbidity, chemical oxygen demand (COD) and metals. Digestion process was first conducted to recover the iron, followed by jar test to determine the performance of the recycled coagulant.

The effectiveness of the RIS coagulant is evaluated on three types of treatment, which are the leachate from Kelantan landfill, turbidity removal of surface water and the treatment of Melaka petroleum refinery waste.

# CHAPTER 2

# LITERATURE REVIEW AND THEORY

## 2.1 Coagulation process

Coagulant is insoluble particles and chemicals added to waters to enhance coagulation process. The principal chemicals used for coagulation in water treatment are inorganic metal compounds as alum and ferric chloride, prehydrolized metal salts and synthetic organic coagulants. Coagulant such as alum, ferric chloride and ferric sulfate hydrolyze rapidly when mixed with the water to be treated. As the chemicals hydrolyze, they form insoluble precipitates that destabilize the particles by neutralizing the charge on fine particles or adsorb on the surface of the particulates and reduce the repulsive forces and/or form bridges between them. Natural or synthetic organic polyelectrolytes are also used for destabilization of particles, which allows the particles to agglomerate [5]. The theory of the coagulation reactions is complex because of the many competing reactions. Therefore, the simplified reactions used to describe the various coagulation process can only be considered approximations, as the reactions may not necessarily proceed as indicated [6].

Recently, inorganic polymer flocculants (IPFs) or prehydrolyzed metal salts have been developed rapidly. IPFs are prepared by reacting alum or ferric with various salts and water and hydroxide under controlled mixing conditions [7]. Among them is polyaluminum chloride (PACl) and has become most widely applied. PACl is less acidic product and may be preferred in naturally acidic location. PACl had consistently less effect in reducing pH than alum. IPFs are actually clusters or aggregates of a combination or intermediate products with various anions, during hydrolysis of metal salts [7]. PACl have molecular weight and size for an aggregating action and its stability to resist further hydrolysis are still much lower than those organic polymer flocculants. However, PACl weaken charge effectiveness in coagulation process or become unstable when stored for longer time [8].

Organic polymeric coagulants have found increasing application, these water soluble cationic polymers mainly used for treatment of waste water. Moreover, the concentration of organic coagulants required for water treatment are significantly smaller than those of mineral compounds and can be used in a wide pH range and don't affect the acidity of the medium [9]. The most widely used organic coagulants are (zetafloc LP526 polyamines) and poly2-hydroxypropyelenedimethylamimmonium chlorides.

Ferrate (VI) salt has strong oxidizing potential and generates of ferric coagulating species and removes suspended or colloidal particulate materials in a single dosing and mixing unit process [10]. Ferrate (VI) ion has the molecular formula, $FeO_4^2$ and it can be prepared by three methods which are dry oxidation, electro-chemical method, and wet oxidation. Among these three methods, preparation of ferrate by wet oxidation method might be the simplest. The wet oxidation method involves the oxidation of a ferric containing solution to form ferrate (VI) solution under high alkaline conditions [10, 12]. Then, ferrate can destabilize the colloidal particles within 1 minute and less residual turbidity treated, whilst ferric and ferrous salts can only achieve the destabilization after 30 minutes mixing [12].

## 2.2 The use of Bittern as a natural coagulant

Bitterns is a by products of solar salt production and found to be effective and economic coagulants for municipal waste water. Seawater dry bittern was found to be an effective and economic source of magnesium and removal turbidity and also suspended solids up until 99 %, whilst the COD removals reached up until 90 %. Jar test experiments can be conducted for coagulation and flocculation tests. Magnesium salts present in the liquid bittern and dry bittern proved to be good coagulants for the treatment of municipal waste water when applied in doses ranging from 0.027 to 0.135 mg/L for liquid bittern and ranging 0.957 to 4.7 mg/L for dry bittern after alkalization with calcium hydroxide or sodium hydroxide to pH of 11.5 [11].

## 2.3 The use of tannin as coagulant

Tannins are phenolic compounds that precipitate proteins. They are composed of a very diverse group of oligomers and polymers. Tannins are high molecular weight polycyclic aromatic compounds that can be used as a coagulant aid to bridge the coagulated particles formed when aluminum or iron salts have been used as the primary coagulant [13]. Tannins can be found in the leaves, fruits, barks, roots, wood trees, etc. Ozacar and Sengil compared the usage of tannin as coagulant and coagulant aids the results showed that tannins operated much better as coagulant aid than as a primary coagulant. It can reduce the amount of required alum significantly. It was found that tannin could be used as a coagulant aid in waste water treatment. The effectiveness of tannin as coagulant aid was demonstrated in reducing turbidity down to $<0.02$ FTU.

## 2.4 Modified clay coagulants

The use of clays as coagulants for waste water treatment was investigated by Jiang, Zend and Pierce. Raw clays montmorillonites K10 and KSF were modified by polymeric aluminum (Al) or ferric and or Al/Fe mixed polymeric species [14]. Natural mineral clays posses specific surface chemical properties such as cation exchange capacity, and adsorptive affinity for some organic and inorganic compounds, which can be a potential adsorbent for treating heavy metals and organic pollutants.

Natural coagulant clays have been used as coagulant aids for improving the settling performance when suing metal based coagulants to treat low particle content water (Nemerow, 1978). By replacing the natural inorganic exchange cations with alkylammonium ions, clay surfaces are converted from being primarily hydrophilic to hydrophobic, which enable them to interact strongly with organic vapours and organic compounds dissolved in water (Zhao and Vance, 1998).

## 2.5 Dewatered sludge from water treatment plant in Kelantan

In Kelantan's water treatment plant, the raw water was obtained from groundwater source. Thus, the treatment used was generally aimed to remove the inorganic iron, manganese, hardness and undesirable gasses in the groundwater. The water was pumped out from the underground well into the tank containing lime for removal of hardness, and both $Fe^{2+}$ and $Mn^{2+}$. There were two stages of aeration process in this plant which are the cascade aerator and the fine bubbles diffused aerator (FBDA). The water flowed into the cascade aerator where lime is added at 300 kg for every 4 hours, together with addition of chlorine at 22 kg per hour. Raw water with excessive soluble iron content was further oxidized in FBDA before flowing into the aeration tank. Chlorine and polymer were added to the water treated in the aeration tank when the volume reaches 3000 $m^3$ per hour. Two blowers were installed to oxidize the dissolved iron and manganese.

Later, alum and polymer were added to the water flowing into the flash mixing tank to aid the flocculation process. The water, which changed into red in color, took 45 minutes to an hour for its suspended colloidal to form floc. The water was then introduced into the clarifier tank, where the floc settled to the bottom of the basin by gravity separation. Finally, lime is added to the treated water in the contact tank to adjust the pH to around 7.5 to 8.5. The separated floc or sludge was removed and stored in a designated area before it is disposed back into the river.

## 2.6 Aluminum and Iron Salts Coagulant Recovery

Water utilities that use surface water as a raw-water source commonly use aluminum and iron salts as coagulants. These metal salts are effective coagulants for particulates and some complex dissolved contaminants and is successfully used throughout the industry. Aluminum and iron hydroxide have shown to have elevated solubility under highly alkaline conditions. Thus, there is potential for reuse of coagulant metal and removal of problematic metal hydroxides from sludge for reduction of the volume and mass of sludge being produced for disposal. Acids are widely used for extractions of iron and aluminum coagulant from water treatment plant sludge. The quantity of acid needed for extraction of aluminum and iron from sludge suspensions is affected by coagulant-metal concentration, overall suspended-solids concentration, and presence of other acid-demanding components. If near-optimal recovery of coagulant value is to be achieved, the pH for acidic extractions would ranges from 2 to 3. If the sludge conditioning is the primary objective, then the optimal pH value is near 4 [20].

## 2.7 The use of recycled iron sludge (RIS) as coagulant using clarifier sludge

The digested sludge from Kelantan, or RIS was used as coagulant to treat the clarifier sludge from UTP. The RIS was shown effective for coagulation of high turbidity of sample and in thickening and improving settleability of the sludge to make it more concentrated. This reduced the cost for dewatering and disposal of sludge compared to other chemical coagulants. The study also showed that a small amount of RIS was required for desired results and the economics also favors its application since it was recycled sludge. However, excessive dosage of the RIS coagulant increased the acidity of the water sample, causing the inefficiency to remove COD and turbidity effectively [15].

## 2.8 Palm Oil Mill Effluent (POME) treatments using recycled iron sludge

RIS was found effective for palm oil mill effluent (POME) treatment, especially in removing COD. However, the excess dosage of RIS added causes the COD and TSS to increase and formed oily clogs. The POME treatment was then compared by using different coagulant, which are alum, RIS and $FeCl_3$. RIS is found effective to remove COD and TSS with the lowest optimum dosage compared to $FeCl_3$ and alum. The potential therefore exists for removal of suspended particles from the beneficial reuse of coagulant metal [15].

# CHAPTER 3

# METHODOLOGY

## 3.1 Introduction

The selection of coagulants and their optimum dosage are typically determined using jar test, which permits rapid evaluation of a range of coagulant types and doses. A modern jar test apparatus consists of six batch reactors, each equipped with a paddle mixer. Square-shaped reactors are used to avoid vortex flow, which can occur if circular beakers are used.

## 3.2 Jar test procedures

The purpose of jar test is to simulate the expected or desired conditions in the coagulation-flocculation facilities. Generally the test consists of a rapid mix phase with simple batch addition of the coagulant followed by a slow-mix period to simulate flocculation. Flocs are allowed to settle and samples are taken from the supernatant for parameters measurement. The results of a series of jar tests can be used to determine the optimum dosage and pH for turbidity or suspended solids removal.

In this study, 500 mL of the raw water sample was measured and poured into the reactors, which were then placed in the stirring machine. If circular beakers were used, it should be located so that the impellers are off-center, but clear the beaker wall by about 6.4 mm. The coagulant was added incrementally to each jar using pipet. The multiple stirrers were set to operate at the "rapid mix" speed of approximately 100 rpm for about 1 minute until the coagulant is completely in the water sample. Later, the speed was reduced to 25 rpm for about 20 minutes to keep floc particles uniformly suspended throughout the "slow mix" period. Floc particles were formed as they cluster together in the water sample. The time for the first visible floc formation was recorded. After the slow mix period ended, impellers were withdrawn and the water sample was allowed to settle for 30 to 60 minutes in quiescent condition. Samples were collected from the supernatant for COD, turbidity and pH measurement.

## 3.3 COD test procedures

In the COD test, the oxygen demand of organic matter in the water sample was measured by allowing it to react with a strong chemical oxidizing agent, potassium dichromate solution ($K_2Cr_2O_7$) in sulfuric acid. The test was carried out at high temperatures of 150°C and in the presence of a catalyst (silver sulfate) by using the thermo reactor. The equivalent amount of oxygen required to oxidize the organic matter to carbon dioxide is equal to the COD of the water sample and is determined from the amount of dichromate consumed in the COD test. The results were determined using spectrophotometer after the vials had been cold in the room temperature. The COD test is popular because it takes much less time, which is about 2 hours only. However, the COD test involves the use of toxic chemicals, which must be properly disposed of.

## 3.4 Digestion of sludge procedures

The digestion method was adopted from 'Standard methods for the examination of water & waste water', APHA method: Nitric acid digestion. In order to produce a high concentration of iron recovery from sludge, digestion was required to dissolve the iron.

A 150 mL conical flask or beaker was acid-washed and rinsed with 1:1 acid nitric and distilled water. An amount of dried sludge was added with distilled water before placing it on a hot plate for digestion process. 5 mL concentrated acid nitric ($HNO_3$) was added to the solution. The temperature was kept at slow boil and the solution was allowed to evaporate to the lowest volume possible before precipitation occurs. A ribbed watch glass was used to cover the beaker and minimize contamination. Boiling chips were added to aid boiling and minimize spatter when high concentration levels were determined. The process of heating and adding concentrated $HNO_3$ continued as necessary until digestion was completed when the solution turned into a light- colored, clear solution. The sample must be kept in eye to avoid it dry during digestion. When the digestion process completed, the sample was cooled to room temperature before adding in distilled water until it reached the initial volume of the solution. After the dilution process, the sample was filtered to separate undissolved metal in the solution.

### 3.5 Measurement of metal concentration in water sample

Spectrophotometer was used to determine the concentration of metal contents in the water sample. The method used was USEPA approved to analyze the water and wastewater with a requirement of digesting the water sample prior to the measurement. Dilution was also required for the sensitivity of the equipment is limited to certain ranges which are generally low. Different types of reagent suitable for reaction and forming a colored solution suitable for absorption spectrophotometry were added to the water sample to determine different types of metals present in it. The following table listed the metals measured in this study and their method of measurement details.

| etal | Method used | Equipment sensitivity (concentration) | Reagents used | Indication when metal presents (color) |
|---|---|---|---|---|
| on | FerroVer | 1 to 5 mg/L | FerroVer iron reagent powder pillow. | Orange |
| opper | CuVer® | 0.04 to 5 mg/L | CuVer® 1 Copper reagent powder pillow. | Purple |
| hromium | ChromaVer | 0.01 to 00.7 mg/L | Chromium 1 powder pillow, Chromium 2 Reagent powder pillow,<br>Acid Reagent powder pillow,<br>ChromaVer 3 Chromium Reagent powder pillow. | Yellowish |
| inc | ZincoVer | 0.01 to 2.00 mg/L | ZincoVer 5 reagent powder pillow, cyclohexonone. | Reddish orange, brown or blue. |

Table 1: Measurement of metal using spectrophotometer

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Introduction

Jar test was conducted on different types of raw wastewater to study the effect of coagulant addition on stability of particles in the waste water sample and establish the optimum dosages required for the treatment to be effective. For the first phase of this study, the jar test was conducted to three types of raw wastewater sample, which are:

i. Landfill leachate

   Alum, ferric chloride and RIS coagulant were used in the leachate treatment where COD and pH were measured to the treated water sample for comparison.

ii. Surface water

   RIS coagulant was used to treat the water sample, where turbidity and pH were measured to determine the dosage needed for effective removal of the suspended solids.

iii. Petroleum refinery waste

   Evaluation of optimum dosage required for RIS coagulant to remove COD in the waste water sample.

In the second phase of the study, only petroleum refinery waste was used as the raw wastewater sample. A series of jar test was conducted to determine the optimum pH for the treatment, followed by the evaluation of optimum dosage needed.

The importance of pH is in controlling the concentration of the soluble metal species that will pass through the treatment process. Together with the optimum dosage, the right range of pH at the right operating range will make the coagulant an effective choice to aid destabilization of suspended solids in the wastewater sample.

## 4.2 Leachate Treatment using alum as a coagulant

The raw water sample used was leachate from a landfill in Kelantan. The initial total and soluble COD for the raw sample of leachate were found to be approximately 876 mg/L and 762 mg/L respectively. The pH of the samples ranged from 6 to 8.

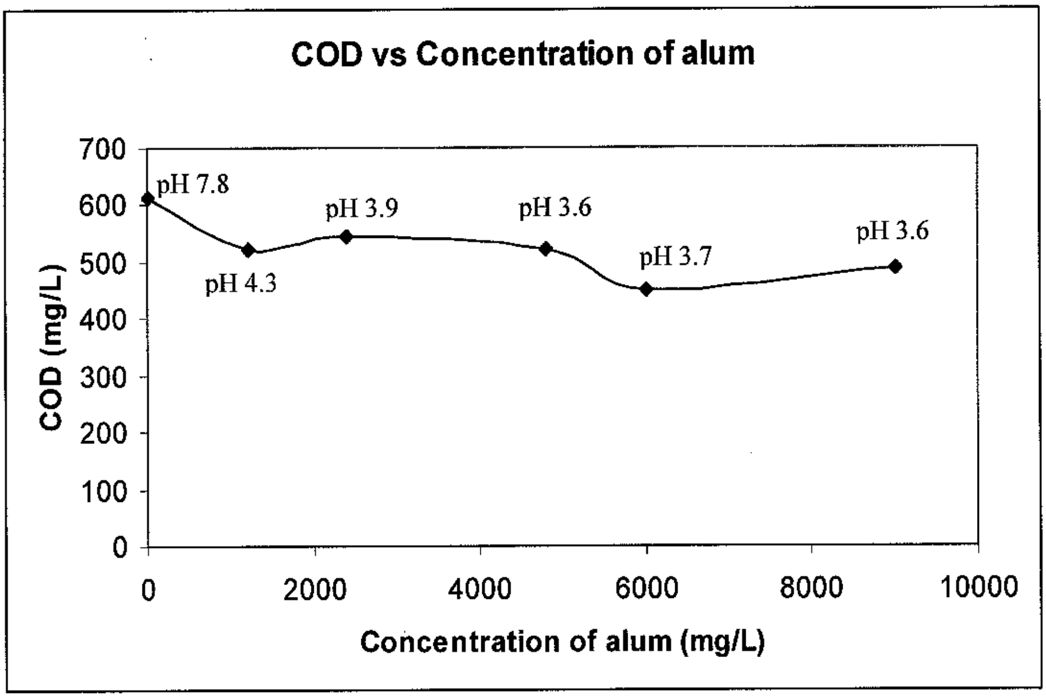


**Figure 1: COD vs. Concentration of alum**

For the first jar test on leachate, Later, alum was added into the wastewater sample, which ranged from 2 to 15 mL. The plotted graph showed the COD removal as a function of alum dose and final COD of the treated wastewater sample. The pH after alum has been added was found to become very acidic, ranged from 3.5 to 4.3. The COD dropped to a range of 487 to 545 mg/L, which was 36% of COD removal. The adjustment on pH should be considered to add supplemental alkalinity to the initial water sample before addition of coagulant, thus achieve the optimum coagulation.

## 4.3 Leachate Treatment using ferric chloride as a coagulant

The initial raw pH of the waswater sample was found to be 7.6 with COD of approximately 536 mg/L. The volume of the ferric chloride added coagulant added ranged from 1 to 8 mL. Thus, the final pH was found to become very acidic, ranged from 1.2 to 2.1. From figure 2, it can be observed that the treated COD have increased with the increase in the concentration of ferric chloride added.

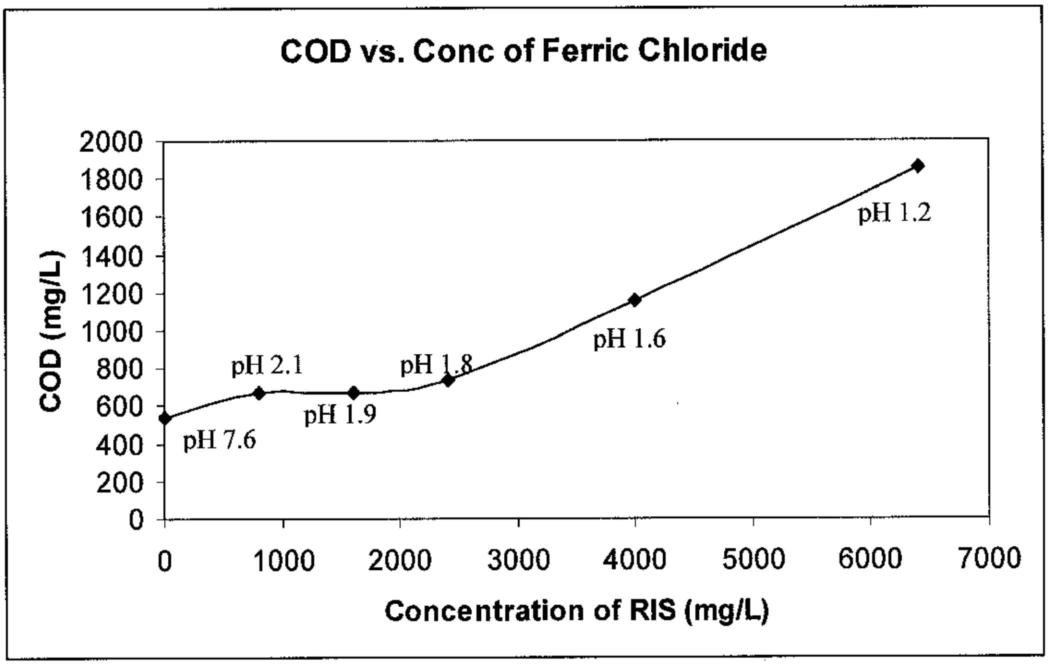


**Figure 2: COD vs. Concentration of Ferric Chloride**

This ineffective treatment may due to the pH of the sample and the ferric chloride itself. In order to obtain the most effective water treatment for removal of COD in the wastewater sample, pH adjustment to the initial wastewater sample to be treated is crucial. For Fe(III) ions, the optimum pH ranged from 5 to 8.5 or more (Amirtharajah and Mills, 1982).

## 4.4 Leachate Treatment using the recycled iron sludge (RIS) as a coagulant

The RIS coagulant was used for the final jar test on leachate. The initial raw pH was found to be 7.9 with COD of approximately 602 mg/L. The volume of the RIS coagulant added to the water sample to be treated was ranged from 2 to 100 mL. From figure 3, it can be observed that the addition of RIS up to 1000 mg/L into the treated water sample slightly reduced the COD to only 8%, and later increased with the addition of the RIS coagulant.

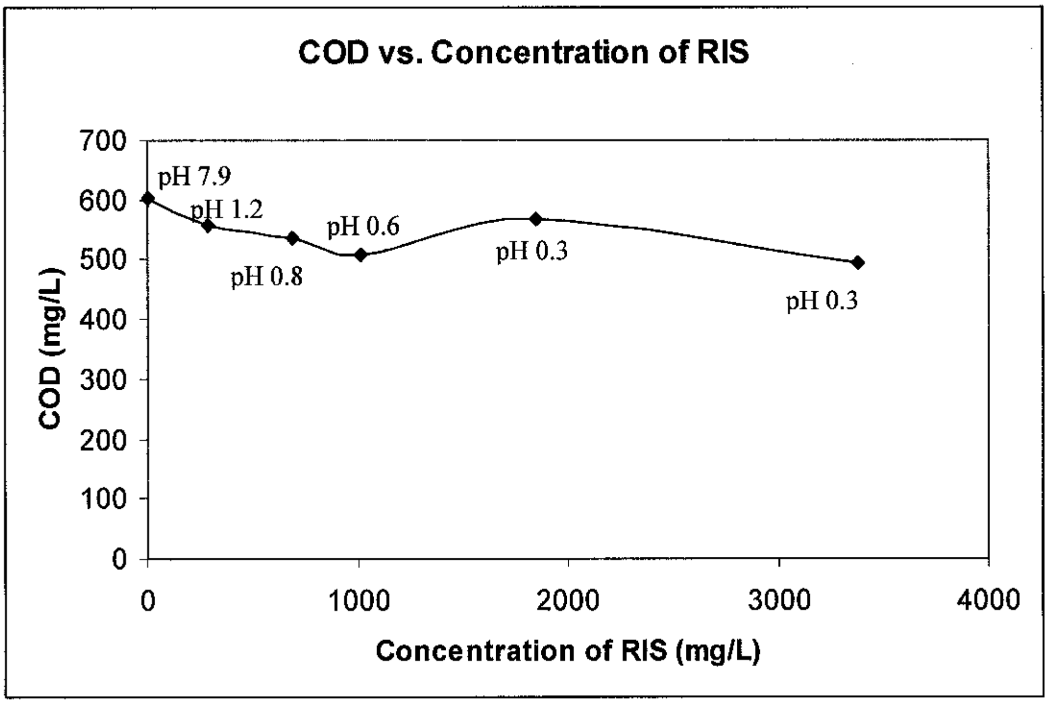


**Figure 3: COD vs. Concentration of RIS**

The final pH of the samples was found to be very low and acidic. This may be due to the fact that metal coagulants are acidic and coagulant addition consumes alkalinity. For low alkalinity waters, the coagulants may consume all of the available alkalinity, depressing the pH to values too low for effective treatment (David J. Pertnitsky, 2003). RIS itself was digested using nitric acid, which significantly contributed to the low pH of the treated wastewater sample when the coagulant is added. Therefore, the pH needs to be adjusted to its optimum value of 9 to 10 prior to the test to achieve effective coagulation.

## 4.5 Turbidity Removal for Surface Water using the recycled iron sludge (RIS) coagulant

The effectiveness of turbidity removal in surface water was evaluated using recycled iron sludge (RIS) as a coagulant. Three jar tests were conducted using 500 mL of samples. The initial pH was approximately 8.1 and the turbidity was found to be 1990 NTU. pH was adjusted using sodium hydroxide (NaOH). The dosages of RIS varied from 10 to 2100 mg/L.

From figure 4, it can be observed that the turbidity and pH of the water samples were decreasing considerably after the RIS coagulant were added. With addition of 1 mL RIS, the percentage removal of turbidity was found to be approximately 95%, with pH 2.5 for the treated water. Meanwhile, the addition of 60 mL of the RIS coagulant removed turbidity up to 97% with final pH of 1.4. The optimal pH was found to be 10.

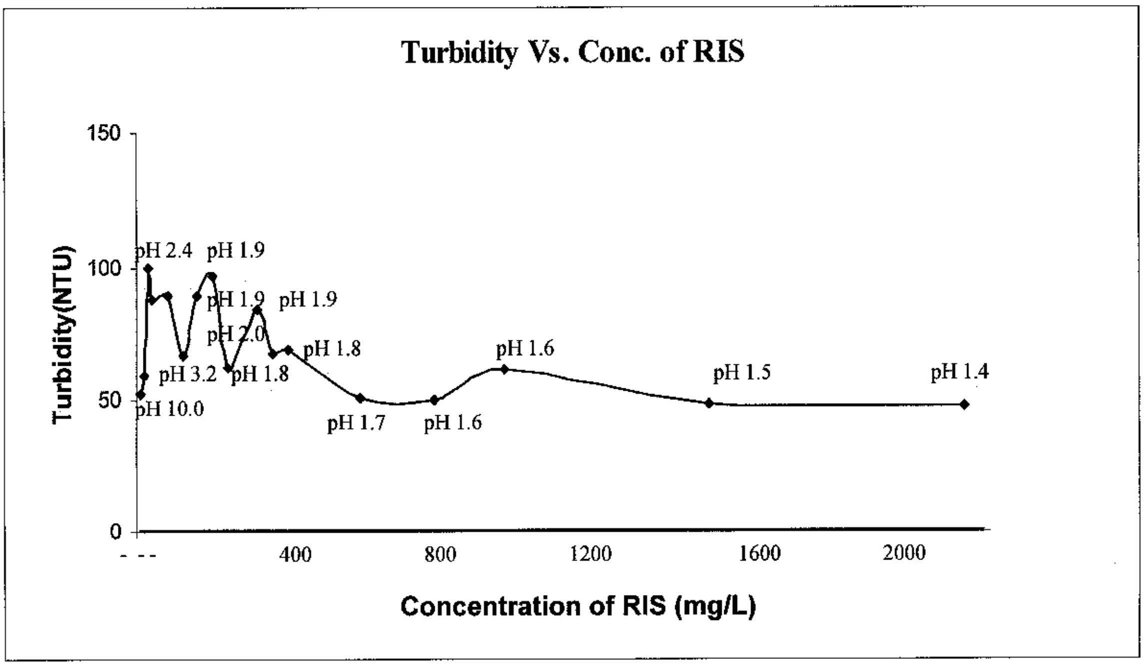


**Figure 4: Turbidity vs. Concentration of RIS**

## 4.6 Treatment of Petroleum Refinery Waste using the recycled iron sludge (RIS) coagulant

Treatment of petroleum refinery waste using RIS coagulant was evaluated. The raw total COD was approximately 850 mg/L with an initial pH of 8.1. The pH was adjusted using various volume of sodium hydroxide (NaOH) with a constant RIS dosage of 40.6 mg/L. The second jar test was conducted with pH adjusted using sodium hydroxide (NaOH) to pH 12. The dosage for RIS added varied from 18.62 mg/L to 311 mg/L. The final pH ranged from 11.8 to as low as 5.8. The final soluble COD ranged from 157 to 437 mg/L.

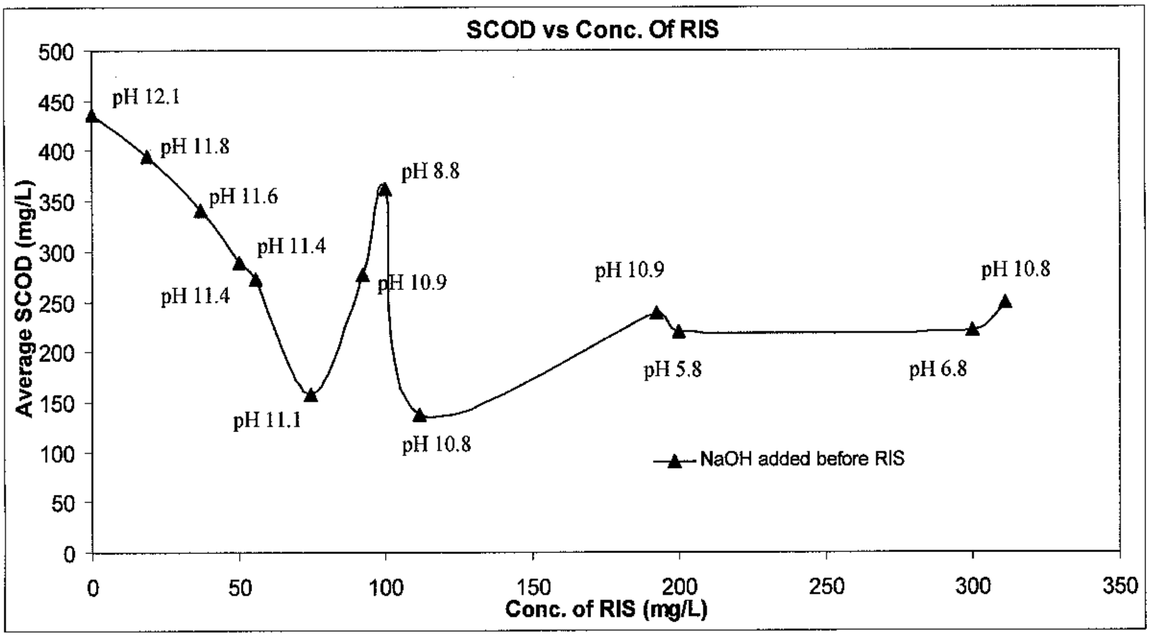


**Figure 5: Average Soluble COD vs. Concentration of RIS**

From figure 5, it can be observed that average soluble COD decreased with the increase concentration of the RIS coagulant added. But at concentration of approximately 75 mg/L, the treatment became ineffective which was shown with the increasing SCOD. At 100 mg/L, the SCOD decreased again with the increasing dosage of RIS, and it was later increased to indicate ineffective treatment when the RIS concentration added increased. Adjustment of pH also plays a vital role in the effectiveness of the treatment itself. Thus, it is found that the optimal dosage of RIS was 114.74 mg/L and the optimal pH is 10.8.

## 4.7 Determination of Optimum pH of alum for the Treatment of Petroleum Refinery Waste

In order to determine the optimum dosage used for treatment of Melaka Petroleum Refinery Waste, jar tests were conducted to first determine the optimum pH to be used in the consequent laboratory experiments. Three jar tests were conducted to each of the coagulant used. The wastewater sample to be treated had an initial pH of 7.1, and COD of approximately 1257 mg/L. Three different dosages of alum and RIS coagulant were used with the initial pH in each beaker adjusted to be in the range of 6 to 12.

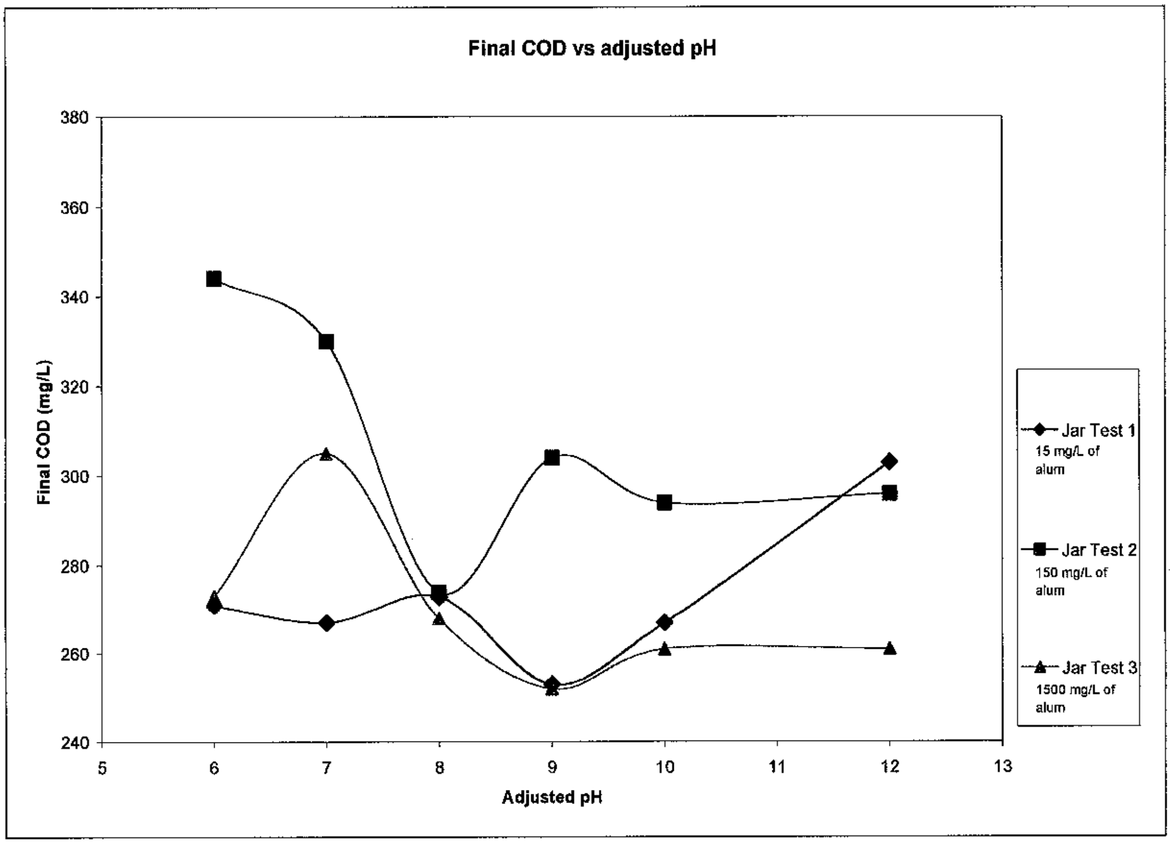


**Figure 6: Final COD (mg/L) vs adjusted pH of alum**

For jar test 1, the COD has the lowest value, which is 253 mg/L at pH of 9. Jar test 2 had the lowest COD at pH 8, which was approximately 274 mg/L. At pH 9, the COD was the lowest for jar test 3, which was approximately 252 mg/L. From the test done, it is concluded that the optimum pH for petroleum refinery waste treatment using alum is in the range of 8 to 9.

## 4.8 Determination of Optimum pH of RIS coagulant for the Treatment of Petroleum Refinery Waste

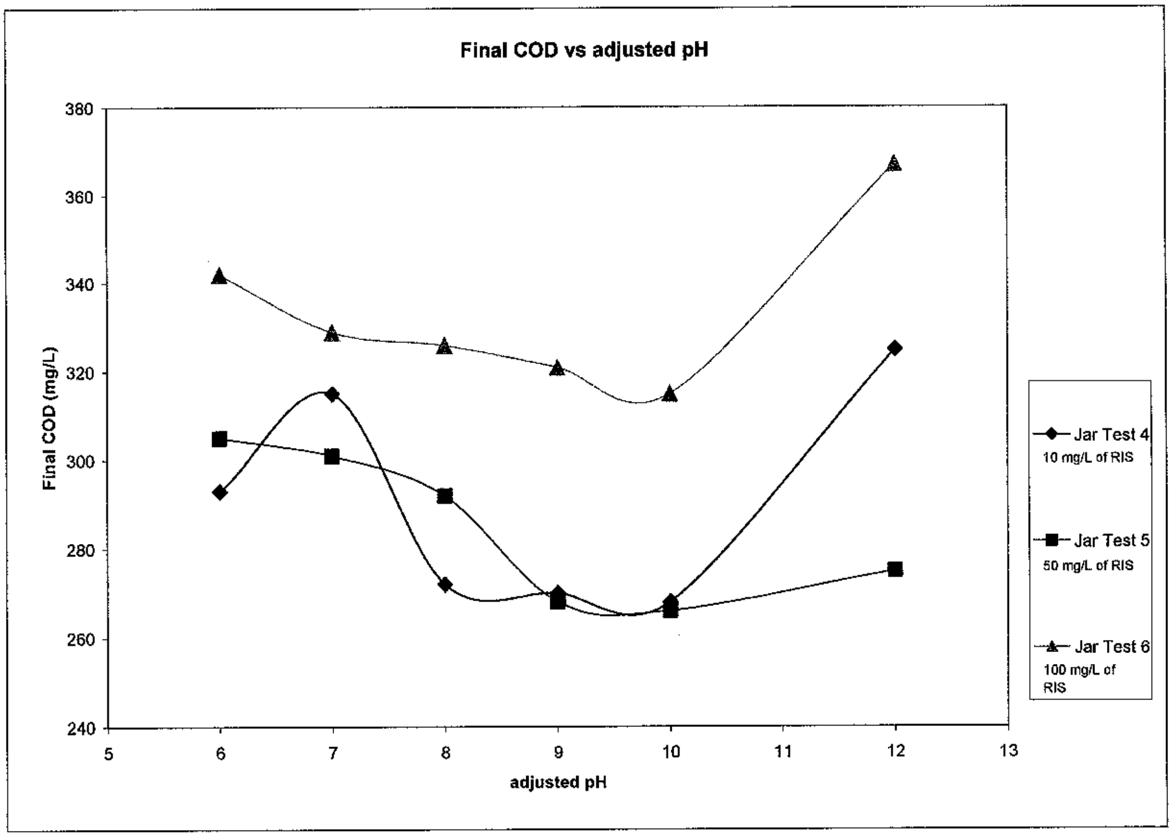


**Figure 7: Final COD (mg/L) vs adjusted pH of RIS coagulant**

COD value was the lowest at pH 10 for jar test using 10 mg/L, 50 mg/L and 100 mg/L of RIS coagulant, which were 268 mg/L, 266 mg/L and 315 mg/L respectively. Thus, the optimum pH of treatment for petroleum refinery waste was found to be at 10.

## 4.9 Treatment of Petroleum Refinery Waste using the Alum

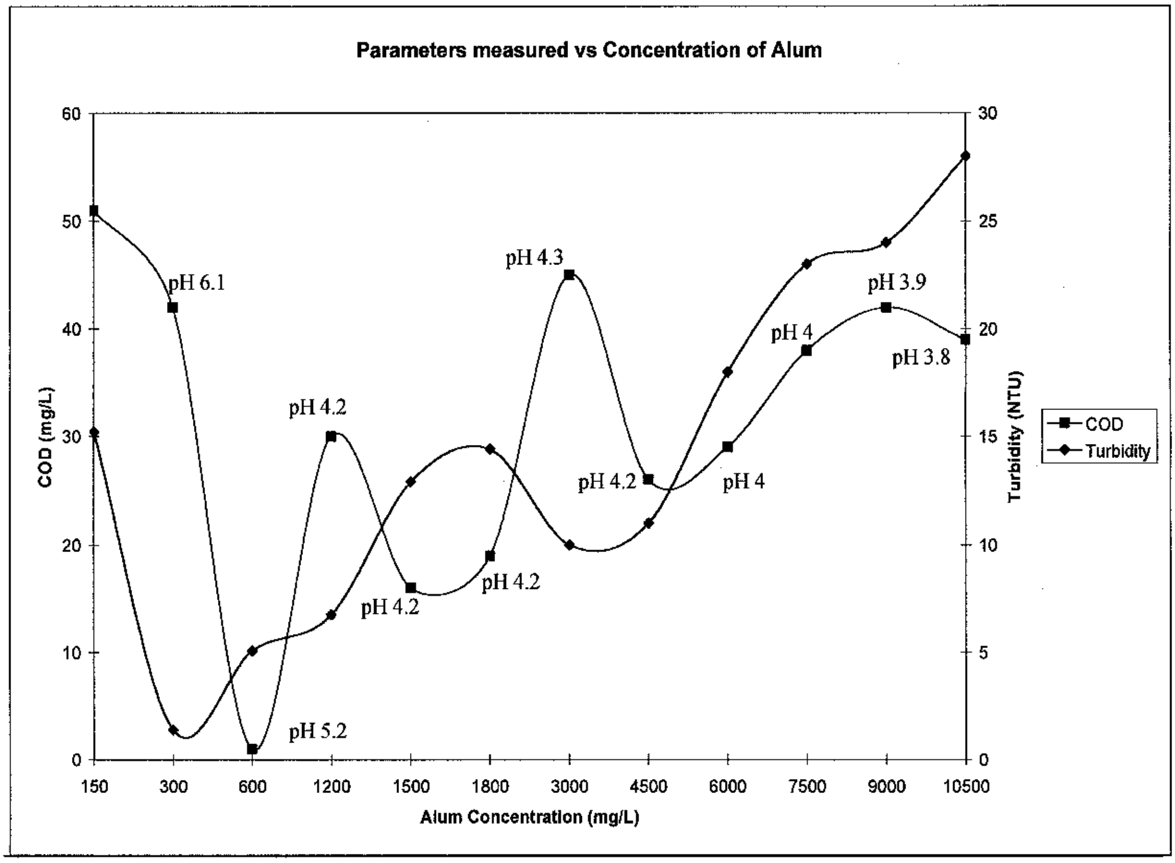


**Figure 8: Final COD/Turbidity vs Concentration of alum**

After obtaining the optimum pH for effective petroleum refinery waste treatment, another test was conducted to obtain the optimum dosage needed for petroleum waste treatment. Two jar tests were conducted with various concentration of alum, ranging from 150 mg/L to 10500 mg/L. No initial pH adjustment was made to the wastewater sample to be treated. The raw water sample was found to have COD of 1176 mg/L, turbidity of 135 NTU and initial pH of 8.3.

From figure 8, it can be observed there was almost complete removal of COD with the addition of 600 mg/L alum into the treated water, with the final pH obtained was 5.2. The turbidity was also removed up to 95% with 300 mg/L of alum added into the water sample.

## 4.10 Treatment of Petroleum Refinery Waste using the RIS

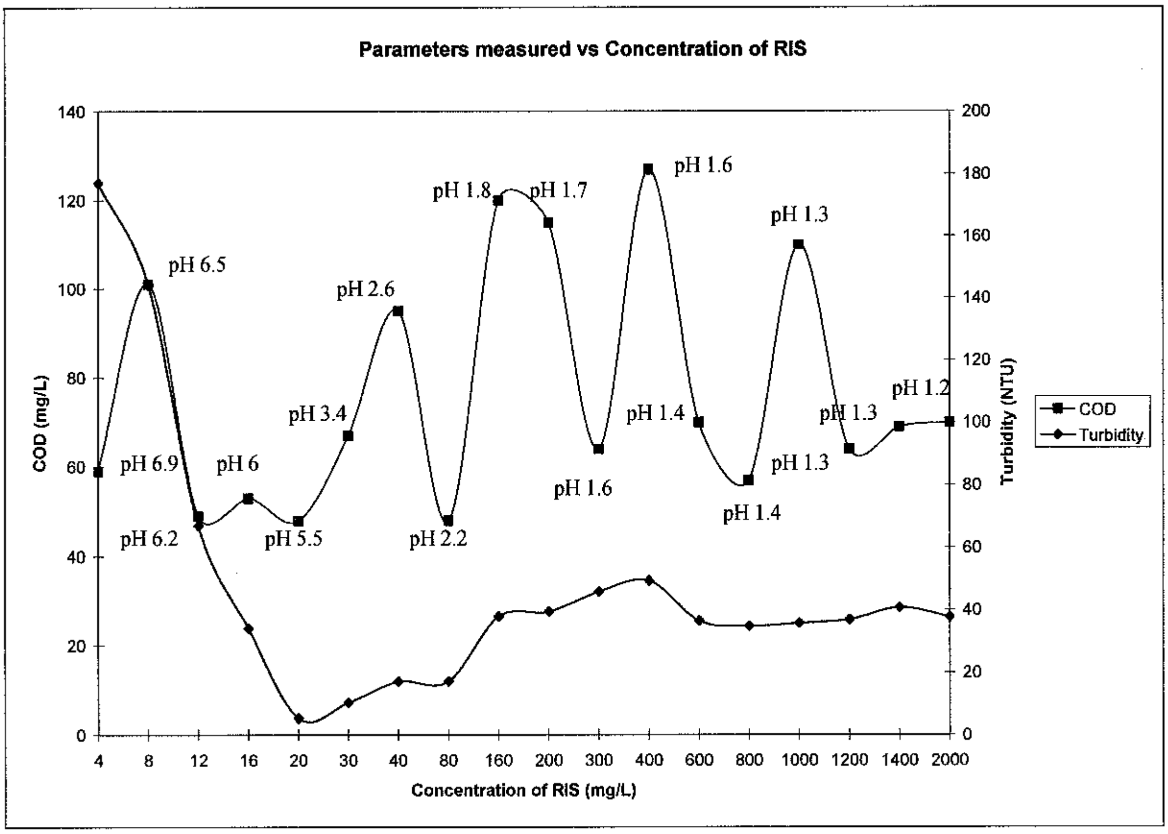


**Figure 9: Final COD/Turbidity vs Concentration of RIS**

Two jar test results were conducted in treating petroleum refinery waste treatment using RIS. No adjustment is made to the initial pH of the water sample and concentration of RIS added into the wastewater sample varied from 4 mg/L to 2000 mg/L. The raw total COD was 1176 mg/L with initial pH of 8.3 and initial turbidity of 135 NTU.

From figure 9, it is found that at RIS dosage of 20 mg/L, the COD and turbidity removal were approximately 96%, with the final pH of 5.5.

Comparing the results of petroleum refinery waste treatment using RIS and alum , RIS is found effective to remove the turbidity and COD as much as alum but with only at a dosage of 20 mg/L, compared to 600 mg/L of alum.

## 4.11 Treatment of Petroleum Refinery Waste using the Alum at optimum pH

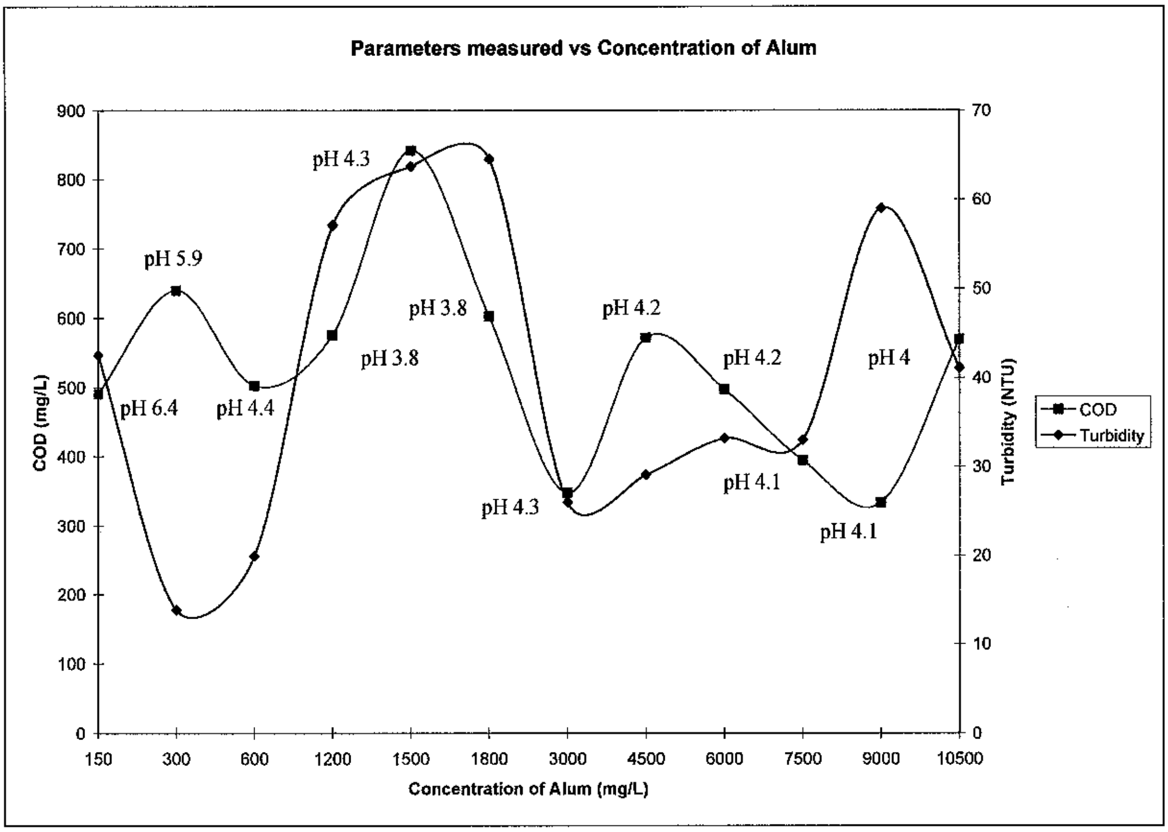


**Figure 10: Final COD/Turbidity vs Concentration of alum**

The petroleum refinery waste treatment using alum was repeated with pH adjustment done on the raw wastewater sample. From the preceding experiments, the optimum pH for alum is approximately at 9. Using the same water sample with raw total COD was 1176 mg/L, initial pH of 8.3 and initial turbidity of 135 NTU, the second set of jar test was conducted with adjustment made to the initial pH to 9. The concentration of alum added into the wastewater sample varied from 150 mg/L to 10500 mg/L.

At alum dosage of 9000 mg/L, the COD reading is at its highest, which was 72%. The final pH recorded at this point is 4.1 and turbidity removal was 56%. Comparing to the optimum dosage of 600 mg/L obtained in the similar jar test using alum as a coagulant but without pH adjustment, it can be concluded that pH 9 may be not effective enough to achieve optimum coagulation. Thus, another test should be conducted to obtain the optimal pH range for treatment of petroleum waste using alum as a coagulant.

## 4.12 Treatment of Petroleum Refinery Waste using the RIS coagulant at optimum pH

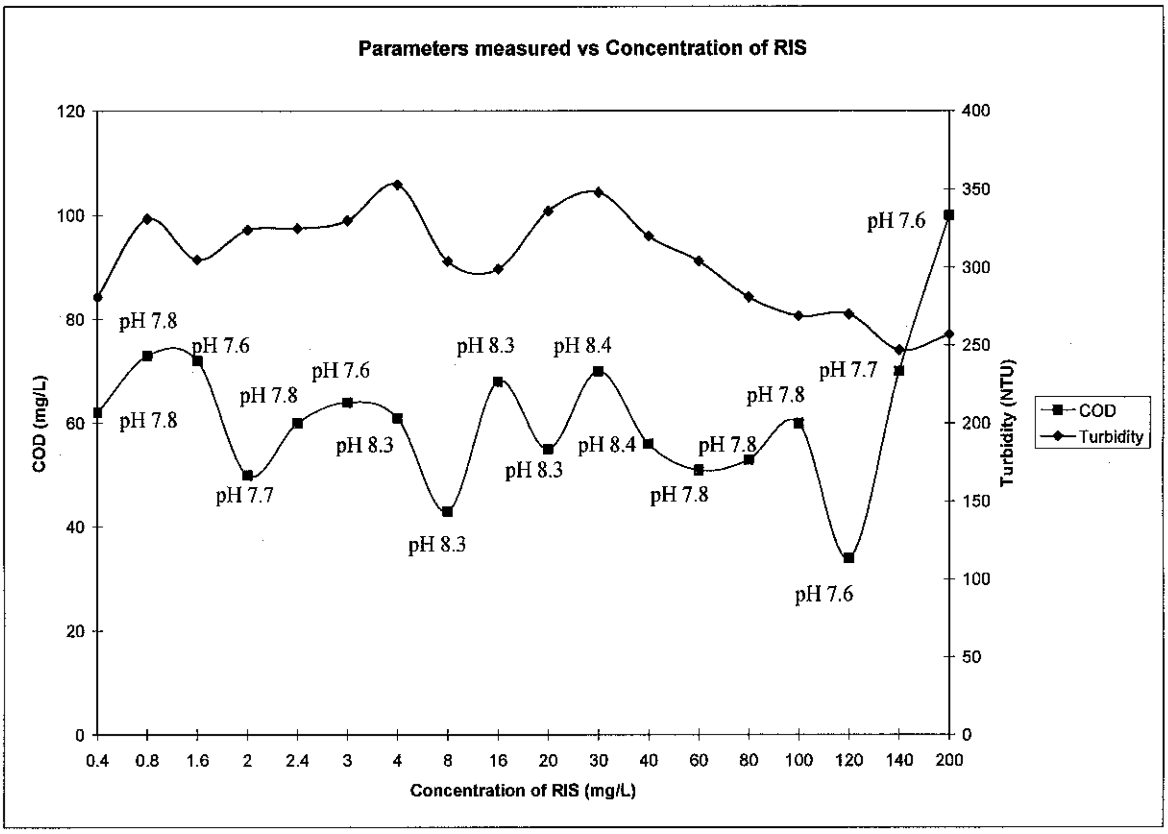


**Figure 11: Final COD/Turbidity vs Concentration of RIS**

The jar test was conducted to treat wastewater sample using RIS as a coagulant. The wastewater sample had a raw total COD of 1176 mg/L, initial pH of 8.3 and initial turbidity of 135 NTU. Addition of sodium hydroxide (NaOH) to the water sample adjusted the initial pH to its optimum, whilst the concentration of RIS added to treat the wastewater sample was varied from 0.4 mg/L to 200 mg/L.

The COD removal was found to be 97%, recorded at the RIS dosage of 120 mg/L, with the final pH of 7.6. The results showed that RIS is effective to remove the COD in petroleum refinery waste water. Optimum pH and dosage were 10 and 120 mg/L respectively.

### 4.13 Removal of heavy metals from petroleum refinery waste using RIS as a coagulant

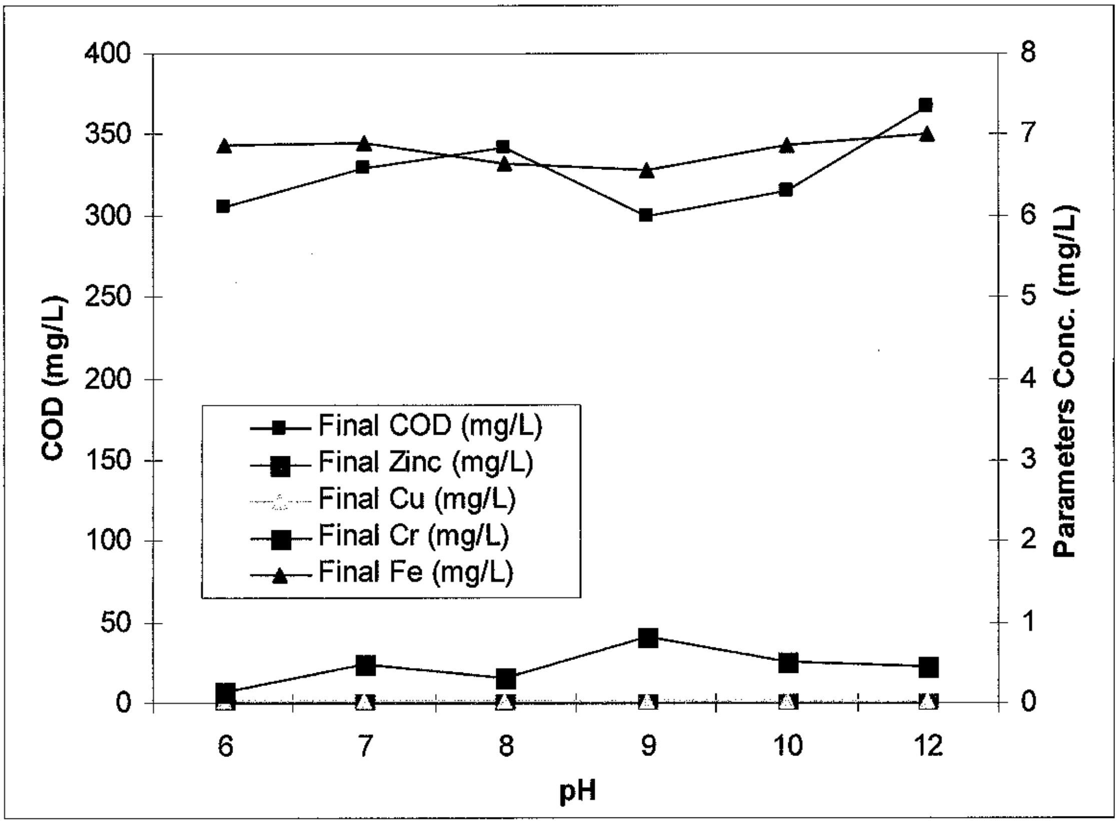


**Figure 12: Final COD/Turbidity vs pH**

A test was conducted to measure the removal of heavy metals within the petroleum refinery wastewater sample. A constant dosage of RIS coagulant at 100 mg/L was added to the wastewater sample. After the jar test, the treated sample was filtered and a portion of it was tested to evaluate the effectiveness of RIS coagulant in removing common heavy metals. The metals measured were namely Zinc, Copper, Chromium and Iron. The selection of heavy metals was done according to the availability of laboratory equipment and chemical reagents used to measure them. The initial raw pH was 7.1, with the initial raw COD, Fe, Zn, Cr and Cu of 1257 mg/L, 3.02 mg/L, 370 mg/L, 1.96 mg/L and 2.01 mg/L respectively. Fe was ineffective to be removed since the addition of RIS coagulant increased the content of iron in the treated sample. Zinc, Chromium and Copper had removal of 99%, 77% and 20% respectively. Further experimental works should be done to evaluate the RIS coagulant potentiality to remove heavy metals in wastewater.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

In this project, raw wastewater samples were taken from three main sources, which are the landfill leachate, surface water and petroleum refinery waste. To evaluate of the effectiveness of the recycled iron sludge (RIS) coagulant compared to other alum and ferric chloride. From the results obtained, comparison of parameters used is in terms of optimum dosage, turbidity, pH and COD.

For leachate treatment, the results showed that the RIS coagulant can be used to treat the waste water sample but the pH must be adjusted to its optimum to avoid treated wastewater sample become too acidic. RIS coagulant is comparable to alum to treat leachate, with a slight removal of COD at 36% for alum and 8% for RIS. The final pH was at a range of 2-1, which indicates that leachate is low alkalinity water, thus causing ineffective coagulation process when the metal coagulant is added.

The turbidity removal of surface water using RIS as a coagulant had shown a significant result in which the addition of 1 mL of RIS coagulant into water sample removed the turbidity to 95%. When the dosage was further increased to 60 mL, the removal increased slightly to 97%. Nevertheless, the final pH was very low since no pH adjustment was made to the initial raw water sample.

For petroleum refinery wastewater treatment, the pH was adjusted to 12 and RIS coagulant was used to treat the samples. It is found that the optimal dosage of RIS for petroleum refinery wastewater treatment was 114.74 mg/L, with the final pH of 10.8.

The second phase of the project was focused on only petroleum refinery waste. A series of jar test was conducted to first determine the optimum dosage to be used in the treatment. The optimal pH for alum and RIS were found to be 9 and 10 respectively.

From the preceding test, the petroleum waste treatment using alum and RIS coagulant were conducted. For treatment using alum as a coagulant and without initial pH adjustment to the water sample, it is found that 600 mg/L of alum removed almost the entire COD in the treated water. 300 mg/L of the same coagulant is needed to remove 95% of turbidity.

The treatment is repeated using RIS as a coagulant, and the results showed that 20 mg/L of RIS removed 95% of COD. Comparing this to the alum dosage, it is clear that RIS is a potential coagulant to effectively achieve the similar removal of COD with only a small dosage required.

Later, the test was conducted again with pH adjustment to the raw wastewater samples. Similar dosages of the coagulants were added into the samples after pH adjustment. Thus, the results indicated that at dosage of 900 mg/L, alum is effective to remove 72% of Cod and 56% of turbidity. As for RIS, 120 mg/L were needed to remove 97% of COD with the final pH of 7.6.

From these three treatments, it can be concluded that the RIS coagulant had shown effective to become a coagulant. Although the pH have directly affected its performance, but from the results shown RIS was the best natural coagulant to be used in treating leachate, surface water and also petroleum refinery waste.

## 5.2 Recommendation

The digestion process of the sludge should be carefully managed. As for this study, the digestion conducted was only at a laboratory scale, where beakers and hot place were used. Constant stirring and addition of acid were also manually handled. Thus, it is more economical and safe if a special equipment or reactor is available to assist the acid digestion process of sludge. Besides that, more research should be done on the application of recycled coagulant and its application in wastewater treatment. Matters such as the typical dosages, optimum pH range and interactions with other constituent in water should be clarified.

## REFERENCES


1. J.Q. Jiang, Z. Zeng and P.Pearce. Preparation and Use of Modified Clay Coagulants for Wastewater treatment. Water, Air and Soil Pollution (158), April 2004 : 53-65
2. Waseem Akhtar, Muhammad Rauf, Iqbal Ali and Nayeemuddin. Optimum Design of Sedimentation Tanks Based on Settling Characteristics of Karachi Tannery Wastes.Water, Air, and Soil Pollution (98), 1997 : 199-211
3. Jia-Qian Jiang, Barry Lloyd. Progress in the Development and Use of Ferrate (VI) Salt as an Oxidant and Coagulant for Water and Wastewater Treatment.Water Research, 2002 : 1397-1408
4. G.EI Diwani, Sh. Ei Rafie. Bitterns as Coagulants for Treatment of Municipal Wastewater. National Research Center
5. Yasuhiko Watanabe and Kazuhiro Tanaka. Innovative Sludge Handling Through Pelletization/Thickening. Water Research (33), 1999: 3245-3252
6. Lynn G. Turner and Roy E. Carawan. Using COD to Measure Lost Product. JWM, March 1996.
7. Dongshen Wang, Wei Sun, Yi Xu, Hongxiao Tang, John Gregory. Speciation Stability of Inorganic Polymer Flocculant (PACl). Colloids and Surfaces Physiochemical Engineering Aspects (243), April 2004: 1-10.
8. B.Y Gao, H.H. Hanhn, E. Hoffmann. Evaluation of Aluminum-Silicate Polymer Composite as a Coagulant for Water Treatment. Water Research (36), February 2002: 3573-3581
9. Dr. S. K. Maiti, Dr. N. C. C. Karmakar and Poonam Shari. Study on Settling Behavior of Coal Washer Effluent. March 2004.
10. V.F. Kurenkov, E.L. Gogolashvili, I.V.Molgacheva and A. I Gaisina. Cationic Polymers as Organic Coagulants in Water Treatment at Heat and Electric Power Plants.Russian Journal of Applied Chemistry (76). June 2003: 1951-1954
11. Metcalf and Eddy. Wastewater Engineering Treatment and Reuse, 4$^{th}$ Edition. McGraw-Hill, 2003.

12. Gray KA, Waite TD. Coagulation and precipitation studies of the ferrate (VI) iron, 1983. 186:48.
13. Mahmut OZACAR, Sengil. The use of tannins from Turkish Acorns (Valonia) in water treatment as a coagulant and coagulant aid. 2002. 255:263.
14. Chi-Yuan Fan, Yuan Ding, Shih-Long Liou. High rate microcarrier weighted coagulation for treating wet weather flow.
15. T.Clark, T.Stephenson. Development of a jar testing protocol for chemical phosphorus removal in activated sludge using statistical experimental design. 1999. 1730:1734.
16. F. Vaezi & F. Batebi. Recovery of iron Coagulants from Tehran water- treatment sludge for reusing in textile wastewater treatment. Iranian J. Public Health, vol.30, Nos. 3-4, 135-138, 2001.
17. Chi-Wang Li, Jr-Lin Lin, Shyh-Fang Kang, Chung-Lin Liang. Acidification and alkalization of textile chemical sludge: volume/ solid reduction, dewaterability, and Al (III) recovery. Separation and Purification Technology, vol. 42, 31-37, 2005.
18. Wei Chu. Lead metal removal by recycled alum sludge. Water research vol. 33, No. 13, 3019-3025, 1999.
19. Kebreab A. Ghebremicheal and Bengt Hultman. Alum sludge dewatering using *Moringa oleifera* as a conditioner. Water, air and soil pollution, Kluwer Academic Publisher. 158: 153-167, 2004.
20. F. Michael Saunders and Michael L. Roeder. Coagulant Recovery: A Critical Assessment, Georgia Institute of Technology, Awwa Research Foundation, 2006.
21. David J. Pertnitsky, Coagulation 101, Associated Engineering, Calgary, Alberta. TechTrain Conference, 2003.
22. Noor Azyyati Binti Awaluddin, Improving Settleability of Wastewater Treatment Plant Sludge Using Natural Materials and Recycled Sludge, Universiti Teknologi Petronas, December 2005.
23. UKWIR Report Catalogue, Biosolids, UK Water Industry Research Limited, October 2004.

# APPENDICES

Date: 8/6/06 (Petroleum Refinery Waste)
Initial pH = 8.3
Initial COD = 176 mg/L
Initial Turbidity = 135 NTU

Jar Test 1 Alum

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume (mL) | 0.5 | 1 | 2 | 4 | 5 | 6 |
| Concentration (mg/L) | 150 | 300 | 600 | 1200 | 1500 | 1800 |
| pH | 6.5 | 6.1 | 5.2 | 4.2 | 4.2 | 4.2 |
| Turbidity (NTU) | 15.2 | 1.4 | 5.08 | 6.76 | 12.9 | 14.4 |
| COD (mg/L) | 51 | 42 | 1 | 30 | 16 | 19 |

Jar Test 2 Alum

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume (mL) | 10 | 15 | 20 | 25 | 30 | 35 |
| Concentration (mg/L) | 3000 | 4500 | 6000 | 7500 | 9000 | 10500 |
| pH | 4.3 | 4.2 | 4 | 4 | 3.9 | 3.8 |
| Turbidity (NTU) | 10 | 11 | 18 | 23 | 24 | 28 |
| COD (mg/L) | 45 | 26 | 29 | 38 | 42 | 39 |

Jar Test 3 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume (mL) | 2 | 4 | 8 | 10 | 15 | 20 |
| Concentration (mg/L) | 40 | 80 | 160 | 200 | 300 | 400 |
| pH | 2.6 | 2.2 | 1.8 | 1.7 | 1.6 | 1.6 |
| Turbidity (NTU) | 17.1 | 17.2 | 37.8 | 39.4 | 45.8 | 49.3 |
| COD (mg/L) | 95 | 48 | 120 | 115 | 64 | 127 |

Jar Test 4 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume (mL) | 30 | 40 | 50 | 60 | 70 | 100 |
| Concentration (mg/L) | 600 | 800 | 1000 | 1200 | 1400 | 2000 |
| pH | 1.4 | 1.4 | 1.3 | 1.3 | 1.3 | 1.2 |
| Turbidity (NTU) | 36.4 | 34.7 | 35.7 | 36.8 | 40.7 | 37.7 |
| COD (mg/L) | 70 | 57 | 110 | 64 | 69 | 70 |

Jar Test 5 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume (mL) | 0.2 | 0.4 | 0.6 | 0.8 | 1 | 1.5 |
| Concentration (mg/L) | 4 | 8 | 12 | 16 | 20 | 30 |
| pH | 6.9 | 6.5 | 6.2 | 6 | 5.5 | 3.4 |
| Turbidity (NTU) | 177 | 144 | 67 | 34 | 5.4 | 10.3 |
| COD (mg/L) | 59 | 101 | 49 | 53 | 48 | 67 |

Date: 11/8/06 (petroleum Refinery Waste)
Initial pH = 8.2
Initial COD = 180 mg/L
Initial Turbidity = 708 NTU

Jar Test 1 Alum

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume | 0.5 | 1 | 2 | 4 | 5 | 6 |
| Concentration | 150 | 300 | 600 | 1200 | 1500 | 1800 |
| pH | 6.4 | 5.9 | 4.4 | 3.8 | 4.3 | 3.8 |
| Turbidity | 42.5 | 13.8 | 19.9 | 57.1 | 63.7 | 64.5 |
| COD | 491 | 640 | 503 | 576 | 842 | 603 |

Jar Test 2 Alum

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume | 10 | 15 | 20 | 25 | 30 | 35 |
| Concentration | 3000 | 4500 | 6000 | 7500 | 9000 | 10500 |
| pH | 4.3 | 4.2 | 4.2 | 4.1 | 4.1 | 4 |
| Turbidity | 26 | 29.1 | 33.2 | 33 | 59 | 41.1 |
| COD | 348 | 572 | 498 | 395 | 334 | 570 |

Jar Test 3 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume | 2 | 4 | 8 | 10 | 15 | 20 |
| Concentration | 4 | 8 | 16 | 20 | 30 | 40 |
| pH | 8.3 | 8.3 | 8.3 | 8.4 | 8.4 | 7.8 |
| Turbidity | 353 | 304 | 299 | 336 | 348 | 320 |
| COD | 61 | 43 | 68 | 55 | 70 | 56 |

Jar Test 4 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume | 30 | 40 | 50 | 60 | 70 | 100 |
| Concentration | 60 | 80 | 100 | 120 | 140 | 200 |
| pH | 7.8 | 7.8 | 7.6 | 7.7 | 7.8 | 7.6 |
| Turbidity | 304 | 281 | 269 | 270 | 247 | 257 |
| COD | 51 | 53 | 60 | 34 | 70 | 100 |

Jar Test 5 RIS

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Volume | 0.2 | 0.4 | 0.8 | 1 | 1.2 | 1.5 |
| Concentration | 0.4 | 0.8 | 1.6 | 2 | 2.4 | 3 |
| pH | 7.8 | 7.8 | 7.6 | 7.7 | 7.8 | 7.6 |
| Turbidity | 281 | 331 | 305 | 324 | 325 | 330 |
| COD | 62 | 73 | 72 | 50 | 60 | 64 |

Jar Test 1 Alum 15 mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 6 | 6.4 | 7 | 7.1 | 7.5 | 10.5 |
| Final COD (mg/L) | 271 | 267 | 273 | 253 | 267 | 303 |
| Final Zinc (mg/L) | 6.3 | 6.7 | 10.3 | 2.3 | 4 | 11 |
| Final Fe (mg/L) | 1.87 | 1.79 | 1.43 | 1.09 | 0.16 | 0.02 |
| Final Cu (mg/L) | 0.52 | 0.15 | 0.04 | 0.01 | 0 | 0.03 |

Jar Test 2 Alum mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 5.4 | 5.5 | 7.2 | 9.9 | 9.6 | 11.8 |
| Final COD (mg/L) | 291 | 330 | 274 | 304 | 294 | 296 |
| Final Zinc (mg/L) | 2 | 2.3 | 3 | 6 | 1 | 3 |
| Final Fe (mg/L) | 0.49 | 1.26 | 0.03 | 0.1 | 0.02 | 0.04 |
| Final Cu (mg/L) | 0 | 0.06 | 0 | 0.06 | 0.02 | 0.05 |

Jar Test 3 Alum 1500 mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 4.3 | 4.4 | 4.4 | 4.4 | 4.5 | 5 |
| Final COD (mg/L) | 273 | 305 | 268 | 348 | 261 | 261 |
| Final Zinc (mg/L) | 1.5 | 36.7 | 46.7 | 3.7 | 3 | 2.3 |
| Final Fe (mg/L) | 1.8 | 1.54 | 0.43 | 0.46 | 0.33 | 0.14 |
| Final Cu (mg/L) | 1.79 | 1.84 | 1.74 | 1.68 | 1.1 | 0.09 |
| Final Cr | | | | | | |

Jar Test 4 RIS 10 mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 3.7 | 5.1 | 5.6 | 7.38 | 7.52 | 11.38 |
| Final COD (mg/L) | 293 | 315 | 272 | 299 | 268 | 325 |
| Final Zinc (mg/L) | 63 | 62 | 15 | 13 | 26 | 10.3 |
| Final Fe (mg/L) | 5.52 | 2.11 | 0.66 | 0.02 | 0.8 | 0.09 |
| Final Cu (mg/L) | 0.21 | 0.09 | 0.04 | 0 | 0 | 0 |
| Final Cr (mg/L) | 0 | 0 | 0 | 0.01 | 0 | 0.01 |

Jar Test 5 RIS 50 mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 2.4 | 2.4 | 2.4 | 2.5 | 2.7 | 4.5 |
| Final COD (mg/L) | 305 | 301 | 292 | 268 | 266 | 256 |
| Final Zinc (mg/L) | 2.33 | 3.33 | 4.33 | 5.33 | 2 | 35.33 |
| Final Fe (mg/L) | 6.85 | 6.94 | 6.84 | 6.76 | 6.9 | 0.97 |
| Final Cu (mg/L) | 0.67 | 0.61 | 0.66 | 0.6 | 0.05 | 0.58 |
| Final Cr (mg/L) | 0.01 | 0 | 0.02 | 0.02 | 0 | 0 |

Jar Test 6 RIS 100 mg/L

| Jar | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH adjusted | 6 | 7 | 8 | 9 | 10 | 12 |
| Final pH | 1.81 | 1.75 | 1.73 | 1.72 | 1.76 | 1.99 |
| Final COD (mg/L) | 306 | 329 | 342 | 300 | 315 | 367 |
| Final Zinc (mg/L) | 0.04 | 0.17 | 0.45 | 0.03 | 0.31 | 0.17 |
| Final Fe (mg/L) | 6.88 | 6.89 | 6.64 | 6.56 | 6.88 | 7 |
| Final Cu (mg/L) | 1.25 | 1.85 | 2.07 | 1.51 | 1.43 | 1.46 |
| Final Cr (mg/L) | 0.15 | 0.48 | 0.31 | 0.83 | 0.5 | 0.45 |