REUSE OF FERRIC CHLORIDE FROM PRINTED CIRCUIT BOARD WASTE SLUDGE FOR CONDITIONING AND DEWATERING OF MUNICIPAL SEWAGE SLUDGE

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in 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 undertaken or done by unspecified sources or persons.

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CERTIFICATION OF APPROVAL

Reuse of Ferric Chloride from Printed Circuit Board Waste Sludge for Conditioning and Dewatering of Municipal Sewage Sludge

by

Sharifah Baizulikha Syeid Aminullah Ismail

A project dissertation submitted to the
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(Dr. Shamsul Rahman Mohamed Kutty)

ABSTRACT

Recycled ferric chloride (RFC) from Printed Circuit Board (PCB) waste sludge was used as a conditioning agent for dewatering of municipal sewage sludge. A conventional method of capillary suction time (CST) was used to measure dewaterability of the sludge. The result was compared with other conditioners which are commercial ferric chloride, ferric sulphate, and alum. Result shows that RFC of volume 0.8mL yields the best CST value compared to other conditioners. The supernatant quality of all sludge samples were measured by measuring COD and TSS. Result shows that RFC with volume 0.8mL gives the best COD and TSS value. Chemical precipitation was conducted on sludge with RFC flocs for copper removal at pH9 and the result obtained was 99.76% copper removal efficiency.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND STUDY

Apart from achieving environmental benefit, wastewater treatment and management studies are also done to develop cost effective technologies. One of the major parts of wastewater treatment is solid management. Processing and handling of solids before disposal or reuse is financially equivalent to the cleaning of wastewater (EPA, 1979).

Solids from removed from different wastewater treatment processes may contain microorganisms, non-biodegradable particles of mineral matter, and particles that come naturally from the physic-chemical treatment of wastewater originates sludge in liquid or semisolid liquid form. This means sludge contains all the products that contaminate treated water and has potentially significant threat to the environment if not managed properly. Of the constituents removed by treatment, sludge is by far the largest in volume and the processing and disposal is perhaps the most complex problem facing the engineer in the field of wastewater treatment (Tchobanoglous, 1991).

The sludge resulting from wastewater operations typically contains from 0.25 to 12 percent solids by weight (Tchobanoglous, 1991), depending on the operations and processes used. Sludge has to go through several processes including thickening, dewatering and transport for final use or disposal. Based on EPA 1979, sludge dewatering and disposal systems represents a large and important cost centre for wastewater treatment, and its associated capital and operating cost may be as high as quarter to half of the total cost of wastewater treatment (Karr & Keinath, 1978). Thus, it is necessary to minimise the volume of sludge for reduction of handling, transporting and disposal cost.

Inefficient sludge treatment not only leads to low quality effluent, but also reduces sludge solid content, increases disposal cost and necessitates sludge rework. Dewatering process aims to reduce the water content of sludge. Mechanical assistance helps in increasing the dewatering rate of sludge (Millieux, 2003); however optimizing dewatering performance requires both chemical and mechanical equipment. It is also found that there is a lack of scientific understanding of the dewatering process, as evidenced by the numerous contradictions that exists in the literature (Karr & Keinath, 1978) makes it difficult to find general characteristics that describe a specific sludge in terms of dewatering. Often sludge is conditioned beforehand for optimization of this process, using mineral chemicals such as iron salts and lime, and/or organic chemicals such as cationic polymer flocculants and destabilized particles (Millieux, 2003; Krisnamurthy & Virarachavan, 2003). Research nowadays is oriented towards using natural conditioner coagulants of mineral origin in water treatment, but they have not been able to compete effectively due to increase of organic matter concentration in treated water (Song, Williams, & Edyvean, 2004).

Many characteristics have been reported to be important for sludge dewatering. Floc size is considered as one of the most important physical factors in the dewatering of sludge (Karr & Keinath, 1978; Lawler, Chung, Hwang, & Hull, 1986). Turchiulli & Fargues (2004) demonstrated that conditioned sludge using alum results to larger and more compact flocs than using ferric chloride as conditioner hence the settling rate and has better dewaterabilty. Ferric flocs on the other hand contain bound water about 20% lesser than alum flocs (Turchiulli & Fargues, 2004) and using ferric chloride as coagulant gives better result in effluent quality (Song, Williams, & Edyvean, 2003). Dewatering rate was proven to increase with dosage of conditioning agents (Krisnamurthy & Virarachavan, 2003) however, optimization of dosage is important to ensure no excessive sludge mass increase that can affect disposal cost.

Manufacturing of printed circuit boards (PCB) involves several steps, such as etching, drilling, image transfer and electroplating (Multilateral Investment Guarantees Agency, 2011).One of the main sources of pollution from waste generated is from the etching process of the manufacture. Etching is a process of removing conductive material which is copper, on the film mask of the circuit board according to the circuit pattern. Among the common etchants used in today practice are cupric chloride, ammoniacal, sulphuric peroxide, chromic acid and ferric chloride (Cakir, 2006; Adaikkalam, Srinivasan, &

Venkateswaran, 2002). The most prevalent hazardous waste stream comes from the etching process are waste rinse water and spent etchant that contain heavy metal (Fries, 1999). Etching process from the manufacturing of PCB produces (wet content) 3.14-4.85% of copper and 3.17-4.23% of iron in the waste sludge (Xie, et al., 2009). Presence of residual of these metals in unavoidable in the treated water. Onsite and offsite recycling of waste has been in practice in the electronics manufacturing industries (Fries, 1999; Huang, Xie, & Ma, 2011) and one industrial evaluation explained that treatment of PCB waste sludge by ultrasound produces significant amount of ferric chloride that can be reused back as coagulant material onsite (Xie, et al., 2009).

Waste can be seen as 'raw' material used in wastewater plants. In some cases, waste can be used as reagents to treat other wastes (European Commission, 2006). It is important to ensure the waste/material will be available at the right time to ensure continuity and proper consistent performance of treatment process, since delay may incur associated environmental problems.

1.2 OBJECTIVES AND SCOPE OF STUDIES

Objectives of this research are to assess efficiency of recycled ferric chloride (RFC) as conditioning agent for thickening and dewatering of municipal sewage sludge while achieving environmental benefits of reducing pollution threat and technology cost.

To achieve these objectives, raw sludge characterization of municipal sludge and PCB sludge was done. For municipal sludge, characterization includes finding Mixed Liquor Volatile Suspended Solid (MLVSS) and initial pH. For PCB sludge, which is the RFC, initial copper and iron concentration was investigated. Column settling test and capillary suction time (CST) was done for raw municipal sludge to determine control parameters for sludge treated with coagulants, and subsequent effluent quality analysis were done afterwards.

Jar tests and column settleability tests were done for sludge using commercial ferric chloride, ferric sulphate, alum and RFC as coagulants. Optimum dosage and the settling rates were determined from these tests. Conditioned sludges with varying dosage are also tested for CST values.

The effluent supernatants were tested for quality by measuring pH, TSS, COD, and colour. These parameters were compared with guideline standards as environmental impact measure. For effluent supernatant using RFC as conditioner, copper concentration was measured to see presence of the pollutant.

This study also consists of analysis of quantity and fate of RFC used in the treatment process. After comparing copper concentration with environmental guidelines, a suitable treatment method for new waste inquiry was provided.

CHAPTER 2: LITERATURE REVIEW

2.1 ECONOMIC ASPECTS OF WASTEWATER TREATMENT SECTOR

The reason for treating waste is not always the same and often depends on the type of waste and the nature of its subsequent fate. Some waste treatments and installations are multipurpose. The basic reasons for treating waste are: to reduce the hazardous nature of the waste, to separate the waste into its individual components, some or all of which can then be put to further use/treatment, to reduce the amount of waste which has to be finally sent for disposal, to transform the waste into a useful material.

Waste treatment is typically a high volume low return process (EPA, 1979). A fixed or lowered base price, either for the incoming waste or for the recycled product, has placed the commercial emphasis on maximizing throughput and reducing cost overheads. Cost and price of waste treatment is typically established on the basis of investments and running costs. However, in some cases, prices may be determined by operators at the 'low' end of the market. In some other cases, the prices are fixed by agreement between the waste producer and the waste manager, where these may be different for a particular waste depending on who has produced it. Although there are exceptions, and also particularly for older plants, investment levels have been low, due to the low returns and competition with the low prices of landfills. It is expected that high levels of investment will be required to meet the standards set by the actual regulatory regime.

The industry has generally maximized the constructive use of some waste types to treat other wastes; this is expected to continue, particularly using waste as a raw material (European Commission, 2006).

2.2 MUNICIPAL SEWAGE SLUDGE

The typical composition of untreated domestic wastewater is as described in Table 2-1. The typical operation diagram for independent physical-chemical treatment process is as described in Figure 2-1.

Contaminants	Unit	Concentration		
		Weak	Medium	Strong
Solids, total (TS)	mg/L	350	720	1200
Dissolved, total (TDS)	mg/L	250	500	850
Fixed	mg/L	145	300	525
Volatile	mg/L	105	200	325
Suspended solids (SS)	mg/L	100	220	350
Fixed	mg/L	20	55	75
Volatile	mg/L	80	165	275
Settleable solids	mL/L	5	10	20
Chemical oxygen demand (COD)	mg/L	250	500	1000

Table 2-1. Typical composition of untreated domestic wastewater. (Tchobanoglous, 1991)

In UniversitiTeknologi PETRONAS (UTP), the wastewater treatment plant was designed to support 23000 population equivalent (PE), connecting all pumping systems in UTP. The process flow is as described in Figure 2-2.

This treatment plant pipes water into clarifiers to let sludge settle and then removed. This activated sludge is recycled to the aeration tanks to keep the bacterial process going. Leftover sludge is recycled to the aeration tanks to keep the bacterial process going. Leftover sludge is sent to the digester tanks and aerator tanks for more bacterial processing and then water is recycled for reprocessing.

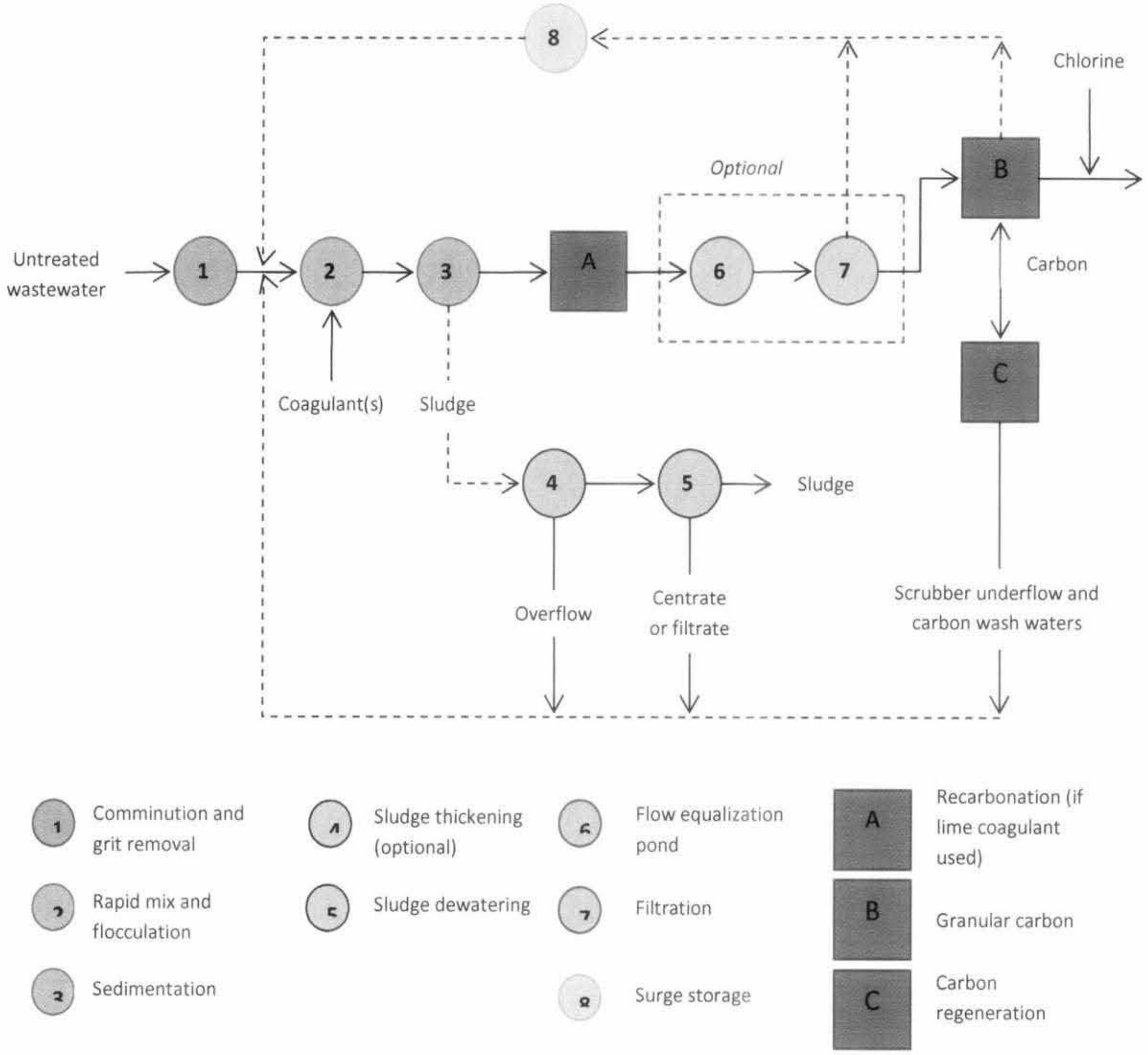


Figure 2-1. Typical flow diagram of an independant physical-chemical treatment plant. (Tchobanoglous, 1991)

All effluent from sewerage and industrial treatment wastewater plant must comply with standards determined by the Department of Environment Malaysia, according to the Third Schedule in the Environmental Quality Act 1974. The standards are as listed in Table 2-2.

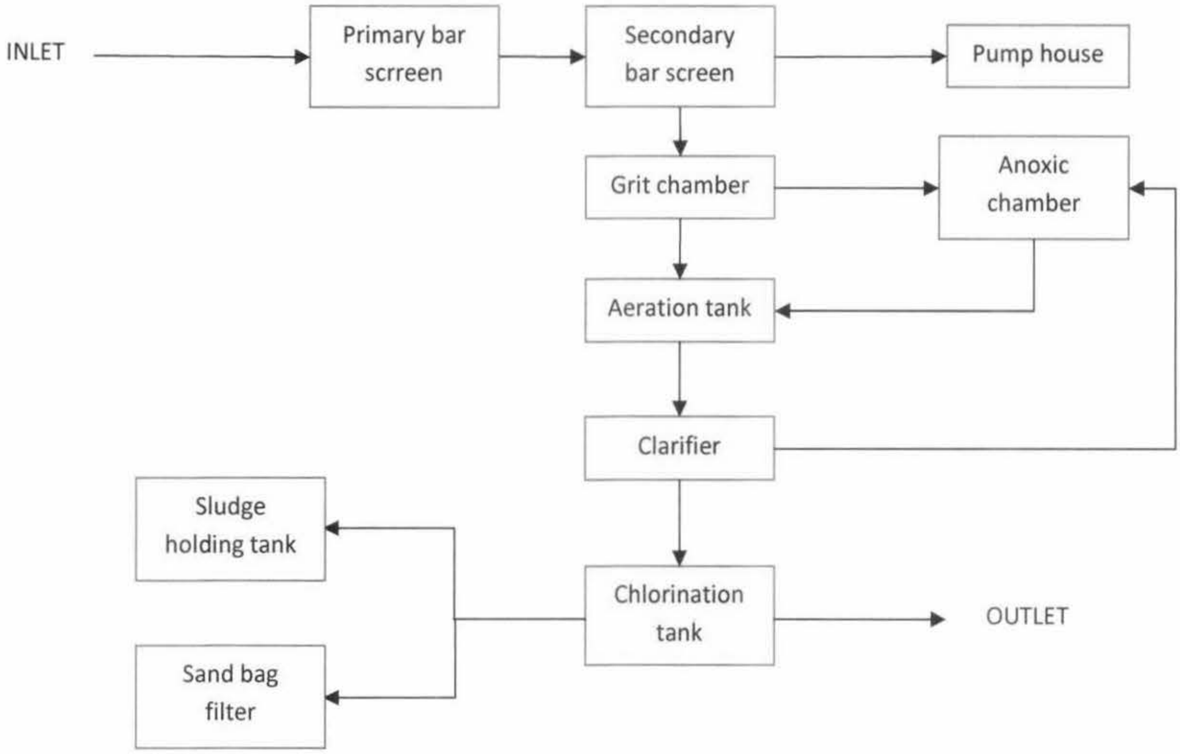


Figure 2-2. Universiti Teknologi PETRONAS sewerage treatment plant process flow chart.

Parameter	Unit	Standard	
		A	B
Temperature	^{0}C	40	40
pH	-	6.0-9.0	5.5-9.0
COD	mg/L	50	50
Suspended solids	mg/L	50	100
Copper	mg/L	0.2	1.0
Iron	mg/L	1.0	5.0

Table 2-2. Parameters limits for Standard A and Standard B of sewerage and industrial effluent according to Environmental Quality (Sewerage and Industrial Effluent) Regulation 1978. (Federal Subsidiary Legislation, 1974)

To design sludge processing and treatment of sludge, the sources, characteristics, and quantities of the solids and sludge to be handled must be known. The sources of solids in a treatment plant vary according to the type of plant and operation method. Listed in Table 2-

3 is the principal sources of solids and the types of sludge generated in wastewater treatment plant.

The characteristics of sludge produced from a treatment plant vary depending on the origin of solids and sludge, the amount of aging that has taken place, and the type of processing that they have been subjected to. Typical data on some of the chemical composition of sludge (untreated and digested) are reported in Table 2-4. The chemical constituent present in sludge is important to determine the ultimate disposal of the processed sludge and the liquid removed from the sludge during processing. The organic content, nutrients, pathogens, metals and toxic organics characteristics of sludge are factors affecting sludge suitability for land application and beneficial use (Tchobanoglous, 1991). Trace elements in sludge are those inorganic chemical elements that can be essential or detrimental to plants and animals (Tchobanoglous, 1991). The terms heavy metals are used to denote several of the trace elements present in sludge. The typical concentrations of copper and iron may vary widely as indicated in Table 2-5.

Typical data on the quantity of sludge produced from various processes and operations are presented in Table 2-6. However it should be noted that quantity of sludge produced will vary widely.

Unit Operation / Process	Types of Solid/Sludge	Remarks
Screening	Coarse solids	Coarse solids are removed by mechanical and hand-cleaned bar screens. In small plants screenings are often comminuted for removal in subsequent treatment units.
Grit removal	Grit and scum	Scum removal facilities are often omitted in grit removal facilities.
Preaeration	Grit and scum	In some plants, scum removal facilities are not provided in preaeration tanks. If the preaeration tanks are not preceded by grit removal facilities, grit deposition may occur in preaeration tanks.
Primary sedimentation	Primary sludge and scum	Quantities of sludge and scum depend on the nature of the collection system and whether industrial wastes are discharged into the system.
Biological treatment	Suspended solids	Suspended solids are produced by the biological conversion of BOD. Some form of thickening may be required to concentrate the waste sludge stream from biological treatment.
Secondary sedimentation	Secondary sludge and scum	Provision for scum removal from secondary settling tanks is a requirement of the US EPA.
Sludge-processing facilities	Sludge, compost, and ashes	The characteristics of the end products depend on the characteristics of the sludge being treated and the operations and processes used. Regulations for the disposal of residuals are becoming increasingly stringent.

Table 2-3. Sources of solids and sludge from a conventional wastewater treatment plant. (Tchobanoglous, 1991)

Item	Activated sludge	Untreated primary sludge		Digested primary sludge	
	Range	Range	Typical	Range	Typical
Total dry solids (TS), %	0.83-1.16	2.0-8.0	5.0	6.0-12.0	10.0
Volatile solids (% of TS)	59-88	60-80	65	30-60	40
Iron (not as sulphide)	-	2.0-4.0	2.5	3.0-8.0	4.0
pH	6.5-8.0	5.0-8.0	6.0	6.5-7.5	7.0

Table 2-4. Typical chemical composition and properties of untreated and digested sludge. (Tchobanoglous, 1991)

Item	Dry sludge, mg/kg	
	Range	Median
Copper	84-17,000	800
Iron	1,000-154,000	17,000

Table 2-5. Typical metal content in wastewater sludge. (Tchobanoglous, 1991)

Item	Specific gravity of sludge solids	Specific gravity of sludge	Dry solids, kg/10^3 m^3	
			Range	Typical
Primary sedimentation	1.4	1.02	108.4-168.7	150.6
Activated sludge	1.25	1.005	72.3-96.4	84.3
Trickling filtration	1.45	1.025	60.2-96.4	72.3
Extended aeration	1.30	1.015	84.3-120.5	96.4*
Filtration	1.20	1.005	12.05-24.1	18.07
Chemical addition to primary sedimentation tanks for phosphorus removal				
Low lime (350-500mg/L)	1.9	1.04	240.9-397.6	301.2**
High lime (800-1600mg/L)	2.2	1.05	602.4-1325.3	795.17**

**assuming no primary treatment*

***sludge in addition to that normally removed by primary sedimentation*

Table 2-6. Typical data for the physical characteristics and quantities of sludge produced from various wastewater treatment operation and processes. (Tchobanoglous, 1991)

2.3 MEASURES OF SLUDGE DEWATERABILITY

Sludge dewatering remains one of the most difficult and elusive of the environmental engineering challenges, yet it is considered indispensable for sludge disposal (Vesilind, 1988). During dewatering, filtrand (a suspension of particles in liquid) is separated by a filter into a filtrate by a pressure difference between the filtrand and filtrate. Interparticle forces and the magnitude of pressure filter cake properties such as porosity and hydraulic permeability (Meeten & Smeulders, 1995) which influence the sludge dewatering characteristics of a given filtrand.

In practice, one of the sludge dewatering aspect that receives much attention is the moisture removal rate, which is controlled by the sludge resistance to the movement of moisture (Lee & Wang, 200). Capillary suction time (CST) test provides an empirical measure of the sludge resistance to the withdrawal of water (Smollen, 1990).

CST test can be used to predict the in-plant performance for centrifugal devices used for dewatering, such as solid-bowl centrifuges, because the performance is governed by the same factors that affect vacuum filters: type and age of sludge, and prior sludge process (Metcalf & Eddy Inc., 1991).

The filtrate was devised by Gale and Baskerville (1968) as a small scale convenient means of measuring dewatering ability of sludge without recourse to an external source of pressure or suction (Meeten & Smeulders, 1995). CST is principally a time period during which a certain volume of filtrate from the sludge is sucked into the filter paper under the sludge head and capillary suction pressure produced by a filtrate and the fibrous matrix of the filter paper (Unno, Muraiso, & Akehata, 1983). A large CST implies poor dewaterability (Turchiulli & Fargues, 2004).

Figure 2-3 shows a schematic diagram of the radial capillary suction time apparatus. A CST apparatus consists of a cylindrical funnel, which is centered in a middle of two concentric electrodes located at radii $R_{1,}$ and R_2, resting on a filter paper. The water is released from the sludge by capillary suction pressure of the paper underneath and spreads out into the filter paper. On reaching a radius R_1, the wetting front starts a clock at time T_1, and stops the clock at reaching radius R_2, at time T_2. In general, the measured CST results are from the combined effects of filter cake and the filter paper (Meeten & Smeulders, 1995).

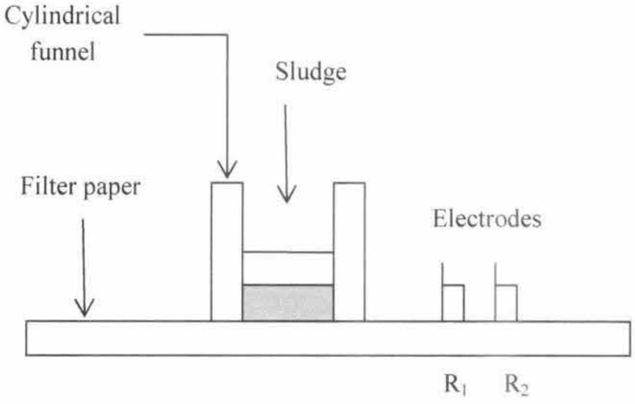


Figure 2-3. Schematic diagram of capillary suction time (CST) device.

2.4 COPPER ETCHING IN PRINTED CIRCUIT BOARD (PCB) MANUFACTURING

In the manufacturing of PCB, basically there are three types of boards: single-sided board, consists of circuits on one side of the board; double-sided boards, consists of circuits on both sides; and multilayer boards which consists of three or more circuit layers. Board manufacturing is accomplished by producing patterns of conductive material on a non-conductive substrate by substractive or additive process with the conductor usually being copper (Multilateral Investment Guarantees Agency, 2011). The substractive process is the preferred route and the steps include cleaning and surface preparation of the base; electroless copper plating; pattern printing and masking; electroplating and etching (Fries, 1999).

Etching is main process to produce circuit patterns on PCB. Historically, the first etchant in PCB manufacturing was ferric chloride, $FeCl_3$, and it is still being used as etchant for small scale production lines. However over the last two decades, new etchants have been introduced for copper etching, and one of them is cupric chloride, $CuCl_2$. Basically, there have been three widely accepted etchants for copper etching, and these are $FeCl_3$, $CuCl_2$, and alkaline etchants. Among all these three etchants, $FeCl_3$ is the cheapest option and has the lowest toxicity due to its lower dissolved copper capacity and it also has the ability of regeneration in the process (Cakir, 2006).

The etching of copper with $FeCl_3$ can be expressed by the following chemical equations:

$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl \quad (1)$$

$$FeCl_3 + CuCl \rightarrow FeCl_2 + CuCl_2 \quad (2)$$

$$2FeCl_3 + Cu \rightarrow 2FeCl_2 + CuCl_2 \quad (3)$$

Effluents from the manufacture of PCB may contain organic solvents, vinyl polymers, stannic oxides, metals such as copper, nickel, iron, chromium, tin, leas, palladium and gold, cyanides; and also sulphates, fluorides and fluoborates, ammonia and acid. In practice, several pollution prevention methods have been adopted by providing alternatives to these processes (Multilateral Investment Guarantees Agency, 2011).

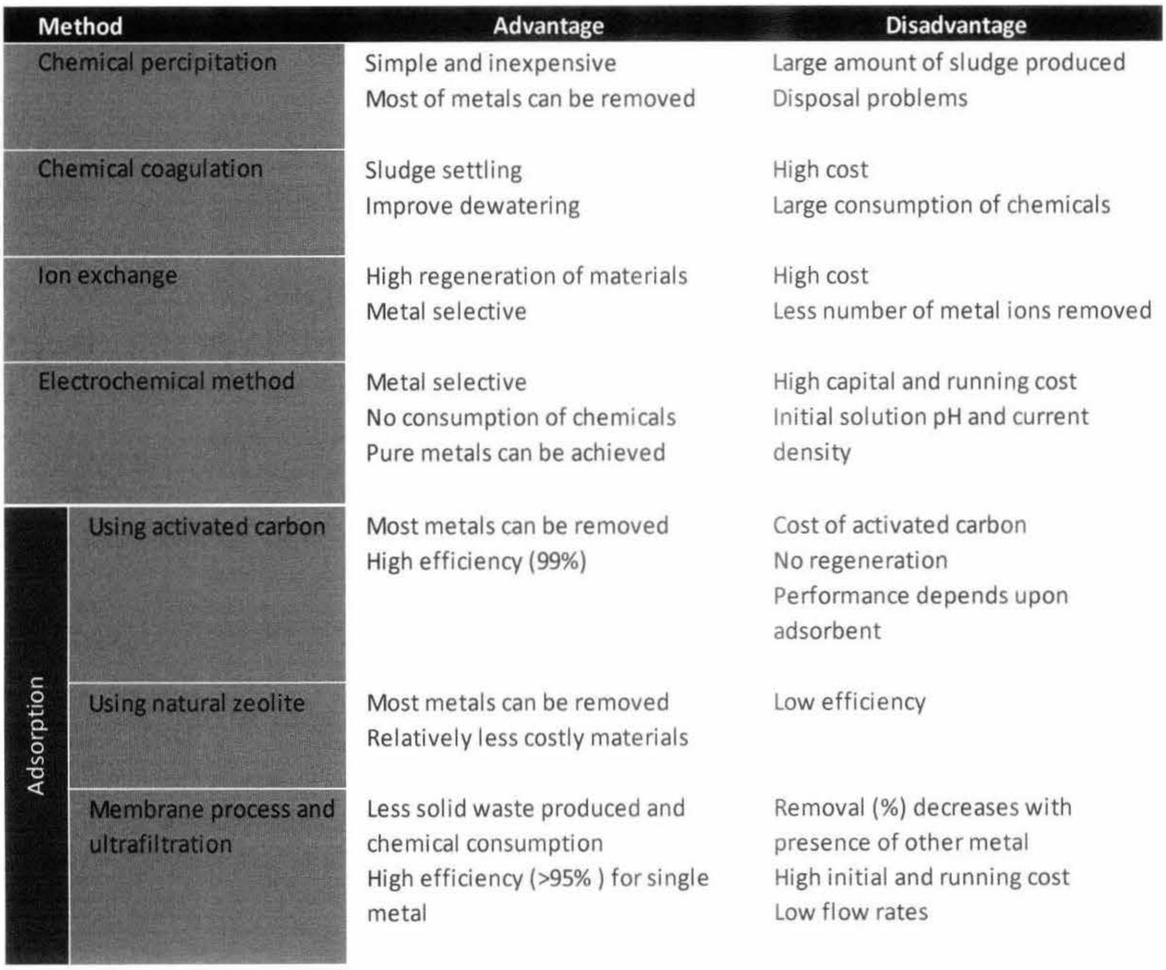
In commercial use, etchants are regenerated to restore their activity, and the dissolved copper is recovered and sold. Several heavy metal waste treatment has been presented (Fries, 1999), and one of them is precipitation using sodium hydroxide, NaOH. The result shows that most of the copper present was removed including nickel and lead (Fries, 1999).

2.5 MEASURES OF HEAVY METAL REMOVAL IN WASTEWATER

Despite being an important constituent for growth of microorganisms, many of heavy metals types are classified as priority pollutants. Thus it is desirable to measure a balance of the concentrations of heavy metals in wastewater, so that it will not interfere with biological importance of wastewater treatment, and the excessive amount of it that will cause pollution. To determine the concentration of these substances vary in complexity according to the interfering substances that may be present (American Public Health Association, 1989).

However these substances can be measured at a low concentration level using instrumental methods such as atomic absorption spectroscopy (Tchobanoglous, 1991).

Since heavy metal ions are non-biodegradable, they can accumulate their amounts along the food chain. Therefore, it is critical necessary to remove or minimize the heavy metal ions in wastewater systematically. A number of methods are already at operation and Table 2-7 presents some frequently-used technologies for heavy metal removal.



Method		Advantage	Disadvantage
Chemical percipitation		Simple and inexpensive Most of metals can be removed	Large amount of sludge produced Disposal problems
Chemical coagulation		Sludge settling Improve dewatering	High cost Large consumption of chemicals
Ion exchange		High regeneration of materials Metal selective	High cost Less number of metal ions removed
Electrochemical method		Metal selective No consumption of chemicals Pure metals can be achieved	High capital and running cost Initial solution pH and current density
Adsorption	Using activated carbon	Most metals can be removed High efficiency (99%)	Cost of activated carbon No regeneration Performance depends upon adsorbent
	Using natural zeolite	Most metals can be removed Relatively less costly materials	Low efficiency
	Membrane process and ultrafiltration	Less solid waste produced and chemical consumption High efficiency (>95%) for single metal	Removal (%) decreases with presence of other metal High initial and running cost Low flow rates

Table 2-7. Comparison of technologies for heavy metal removal from wastewater. (Farooq, Kozinski, Khan, & Athar, 2010)

Precipitation defines a material's ability to go into solution. Materials that are soluble readily dissolve in solution and do not precipitate. Substances that are insoluble do not easily dissolve in solution and stay in their solid form. The goal of metals removal in wastewater is to produce conditions so that metals are insoluble. The formation of metal hydroxides at specific pH values are presented in Figure 2-4.

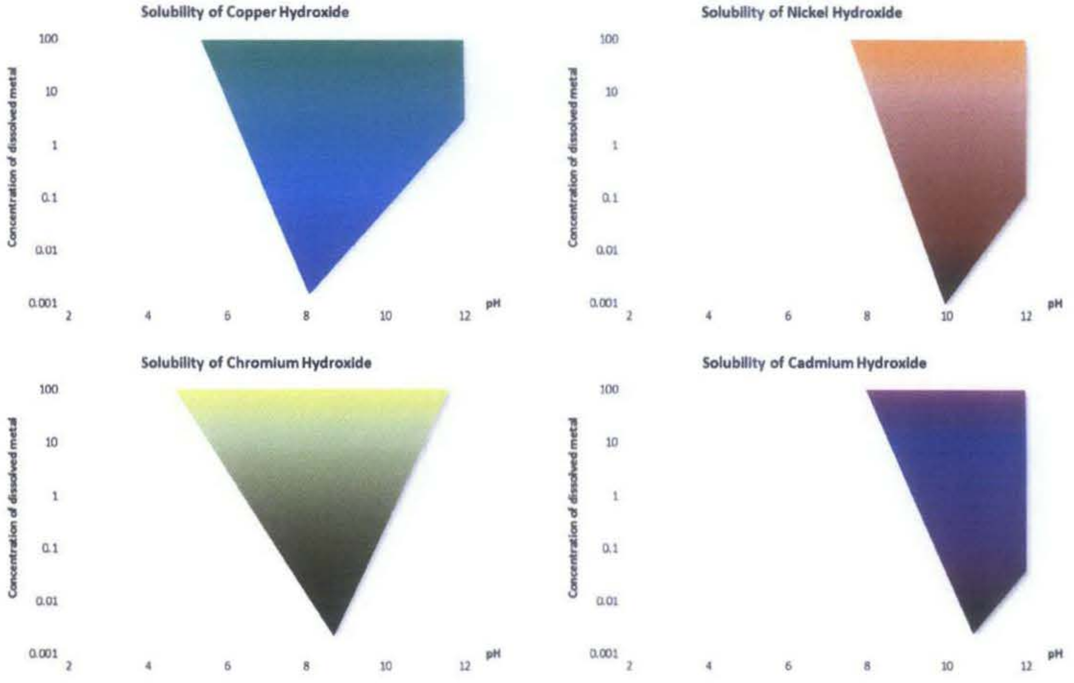


Figure 2-4. Solubility diagram of metalsthrough the formation of metal hydroxides at specific pH values.The region on the solubility diagram indicates the appropriate concentration and pH value for a metal to form a solid precipitate. (pH2O Water Technologies , 2011)

CHAPTER 3: METHODOLOGY

3.1 EXPERIMENTAL APPROACH

The experimental approach of this study is as described in the figure below.

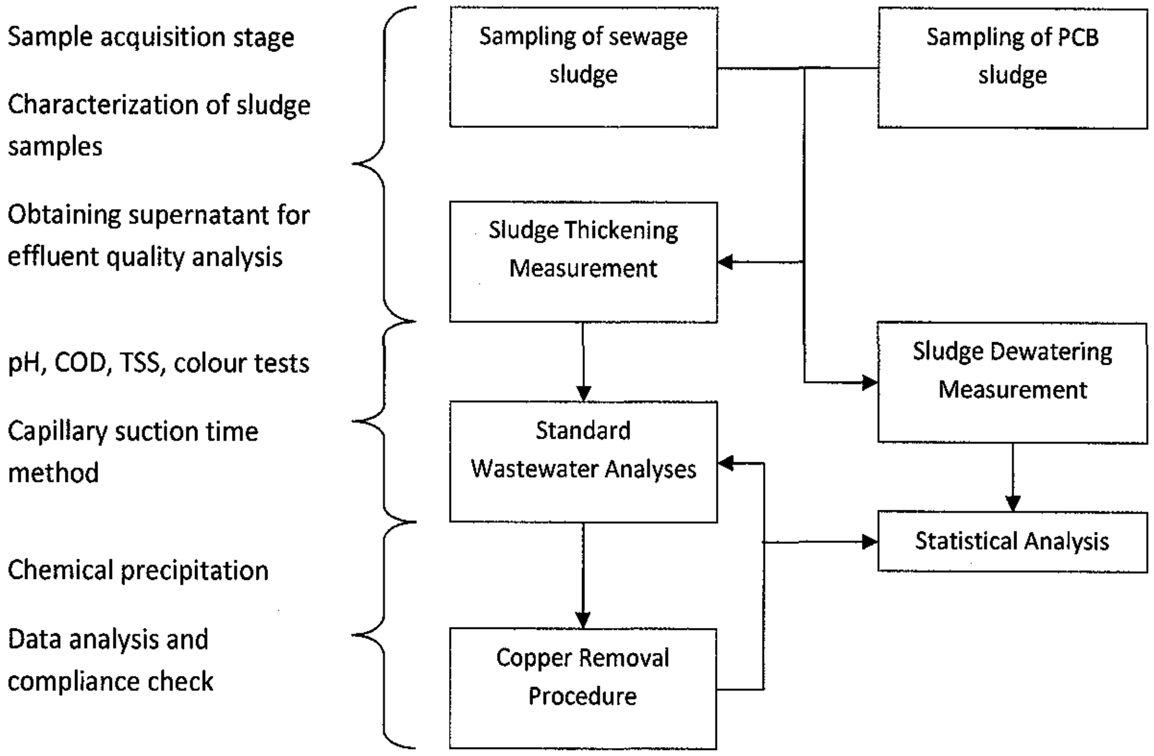


Figure 3.1. Experimental approach flow of the study of reuse of ferric chloride from Printed Circuit Board waste sludge for conditioning and dewatering of municipal sewage sludge.

3.2 SAMPLE ACQUISITION

3.1.1 Sludge characterization

(a) *Sewage sludge*

Digested sludge was taken from Universiti Teknologi PETRONAS wastewater treatment plant from the sludge holding tank. The sludge was brought to measure the Mixed Liquor

Volatile Suspended Solid (MLVSS). MLVSS is the portion of Mixed Liquor Suspended Solids (MLSS) that will vaporize when heated to 600°C. This volatile fraction is mainly organic material and thus indicates the biomass present in the sludge sample. The material that does not vaporize in this test, mostly inorganic substances, is said to be fixed. (Babylon Ltd, 2011) Initial pH of the sludge was measured.

(b) *Printed Circuit Board sludge*

Waste sludge was taken from Universiti Teknologi PETRONAS Printed Circuit Board laboratory. The sample was diluted with dilution factor of 200 and initial copper concentration was measured using Atomic Absorption Spectroscopy (AAS). The sample was preserved in the cold room.

3.1.2 Supernatant characterization

Standard Jar Test procedures was done on the sewage sludge without coagulant as control, and using coagulants of commercial ferric chloride, $FeCl_3$; ferric sulphate, $Fe_2(SO_4)_3$; alum, $Al_2(SO_4)_3$; and waste sludge from printed circuit board, recycled ferric chloride, RFC. The remaining supernatants from each settling column were pippeted carefully and preserved in the cold room. Quality analysis was done on each supernatant sample. Tests for pH, COD, TSS, colour and metal concentration (copper) were conducted. All measurements were performed in duplicate or triplicate.

3.3 SLUDGE THICKENING MEASUREMENT

Coagulation procedure was performed on the sludge using commercial ferric chloride, $FeCl_3$; ferric sulphate, $Fe_2(SO_4)_3$; alum, $Al_2(SO_4)_3$; and waste sludge from printed circuit board, recycled ferric chloride, RFC with varying dosage. All coagulants are of concentration 30%. Coagulation tests were performed in 1L baffled jars. The sludge was under rapid mix for 2 minutes and mixing continued with slow mix for 15 minutes.

Sludge samples were let to settle in 1000mL cylinder with diameter of 6.1cm. Volume of floc settled was recorded in the interval of 30 seconds. Settling heights were calculated using the formula of

$$h = \frac{V}{\pi r^2}$$

Settling heights were plotted against time for each coagulant dosage used. Settling velocity was obtained from each graph plotted. Optimum dosage for each coagulant was determined.

3.4 SLUDGE DEWATERABILITY MEASUREMENT

Sludge samples were shaken hence resuspension of flocs. Sludge dewaterability was assessed by capillary suction time (CST) using the CST apparatus. The apparatus measured the amount of time, in seconds, required for water that has drained out of a sludge sample to travel 1 cm across a rectangular sheet of filter paper Whatman No. 17 chromatographic paper, as initially used by Baskerville & Gale in1967 (Sawalha & Scholz, 2007). All CST measurements were performed in duplicate or triplicate. The use of different coagulants yield different floc concentrations, sizes and distributions, (Karr & Keinath, 1978; Turchiulli & Fargues, 2004; Zhou, 2004; Hou & Li, 2003) thus affecting the values of CST.

CST values were plotted against coagulant dosage for each coagulant type.

3.5 COPPER REMOVAL PROCEDURE

Coagulation procedure was repeated using RFC as coagulant with varying dosage of 0.6mL to 1.0mL. The pH of each jar was adjusted using sodium hydroxide, NaOH and/or sulphuric acid $H_2(SO_4)_3$ until hydraulic precipitation level of copper, Cu, at pH9 was reached. It is found that concentration of Cu in supernatant decreased while pH increased, and although the remnant of Cu concentration in supernatant is lower at pH 10 compared to pH9 (Tu, Chang, You, & Lou, 2010), the latter pH was chosen to be used in this study to ensure the pH can be lower than the regulated effluent standard.

CHAPTER 4 : RESULTS AND ANALYSIS

4.1 SLUDGE CHARACTERIZATION

MLVSS is the portion of Mixed Liquor Suspended Solids (MLSS) that will vaporize when heated to 600°C. This volatile fraction is mainly organic material and thus indicates the biomass present in the sludge sample. The material that does not vaporize in this test, mostly inorganic substances, is said to be fixed. (Babylon Ltd, 2011)

RAW SLUDGE	
MLVSS, mg/L	58656
pH	4.00

Table 4-1.MLVSS and initial pH of raw sludge sample.

Settling test was done and the supernatant of the raw sludge sample were tested for COD, TSS, colour and capillary suction time (CST) measures.

RAW SLUDGE					
TSS (mg/L)	COD (mg/L)	CST(s)	pH		Colour (mg/L Pt)
			initial	final	
125	143	9.25	4.00	4.04	400

Table 4-2. Properties of raw sludge supernatant after settling test procedure.

These values are used as control properties for the procedures that are using ferric chloride 30%, alum 30%, ferric sulphate 30% and recycled ferric chloride as coagulants.

4.2 SETTLING CURVE AND HINDERED SETTLING VELOCITY

Height of cylinder column is calculated using the formula of

$$H = \pi r^2 V \qquad \text{Eq. 4-1}$$

Where r is the radius of the cylinder and V is the volume recorded in the settling test.

Settling height, H, is then plotted against time. Critical concentration point is determined by constructing tangent lines on the flocculant settling region and the compression region of the subsidence curve. These tangents are extended to a point of intersection, and the angle formed is then bisected to the settling curve. The point of intersection between the bisected line and the settling curve is known as the critical concentration, C.

Settling curves of all samples are as shown below.

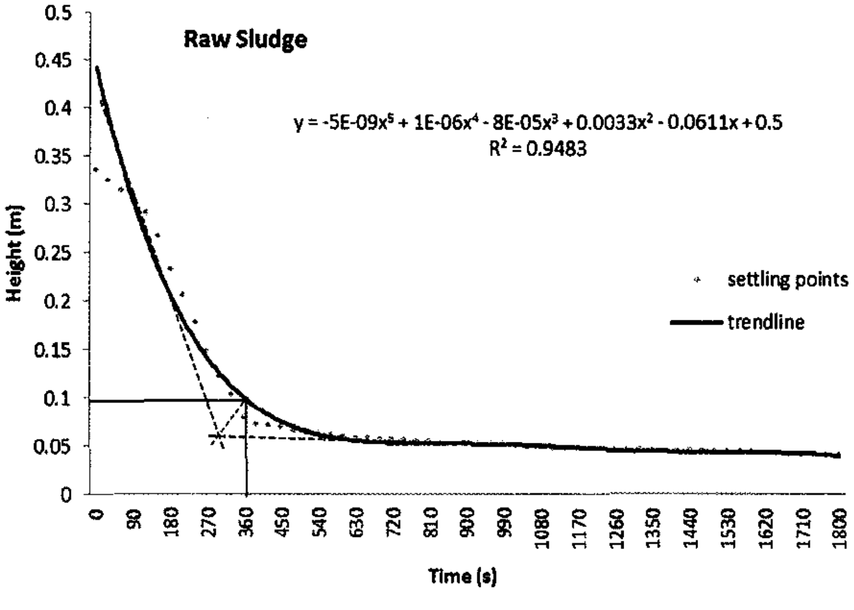
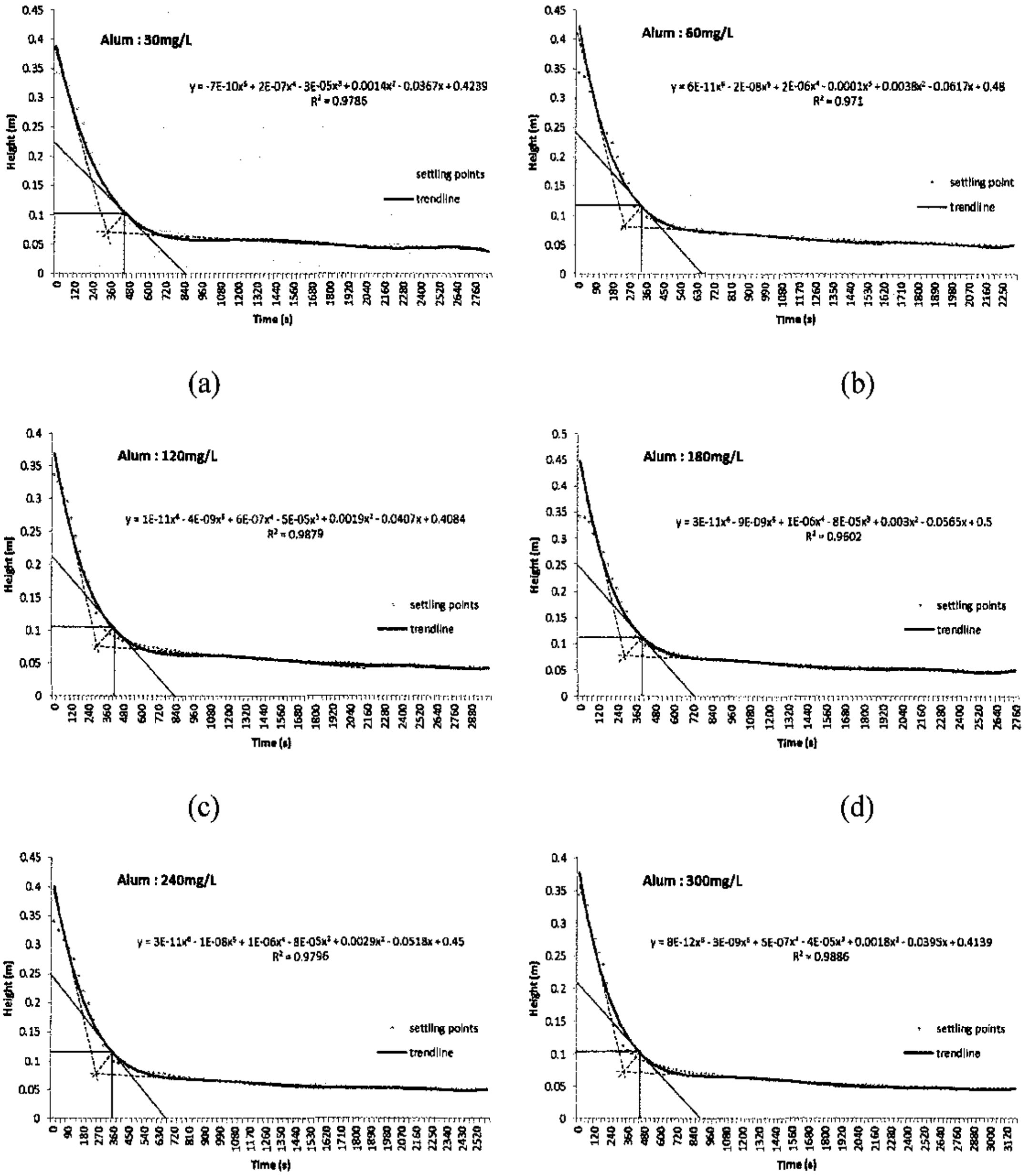


Figure 4-1. Settling Curve of control sludge with no coagulant added.

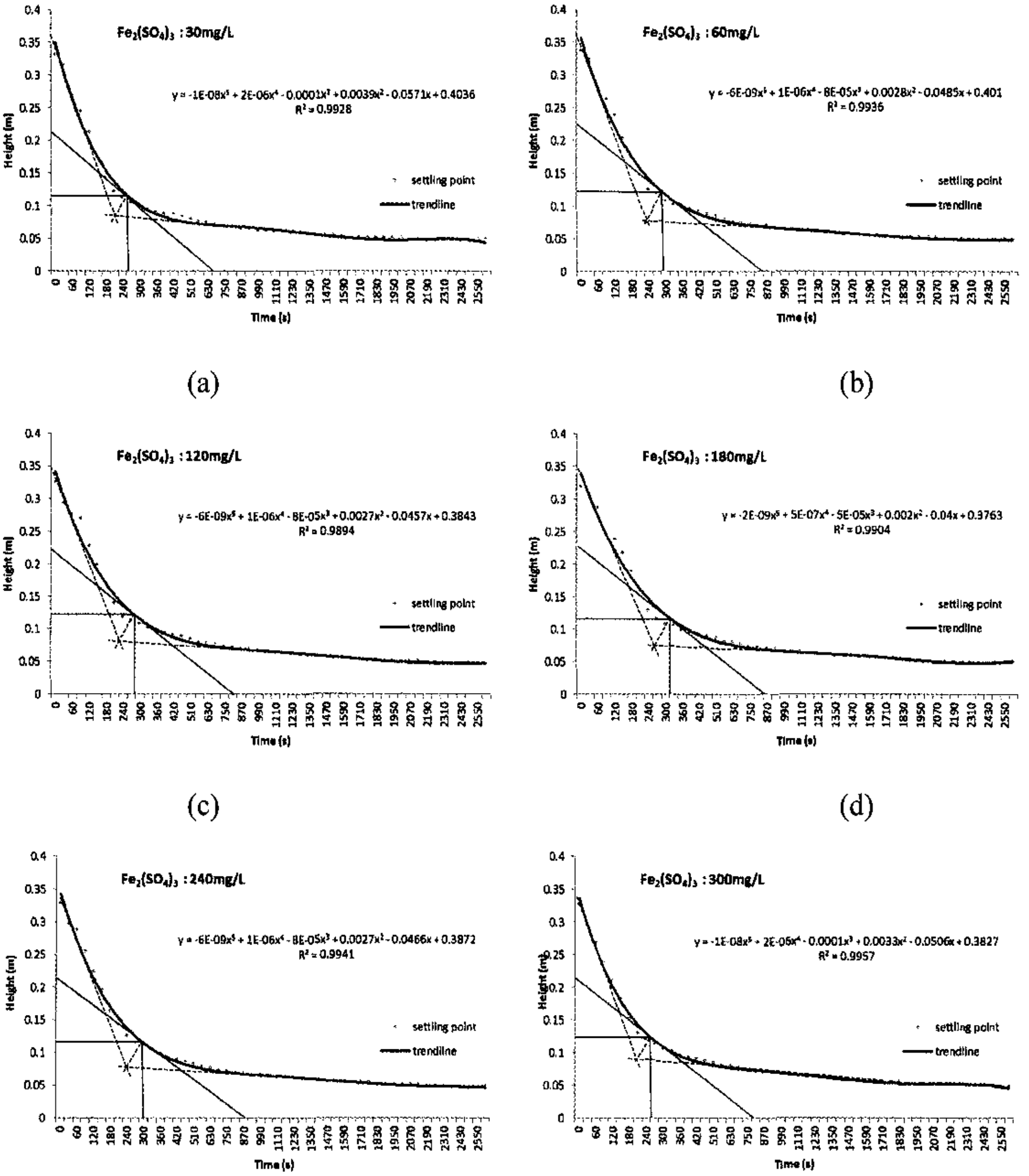


(a) (b)

(c) (d)

(e) (f)

Figure 4-2 (a-f). Settling curves for alum 30% concentration as coagulant with varying dosage.

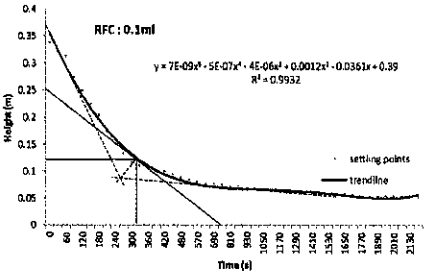


(a) (b)

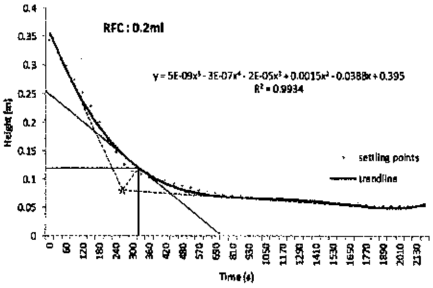
(c) (d)

(e) (f)

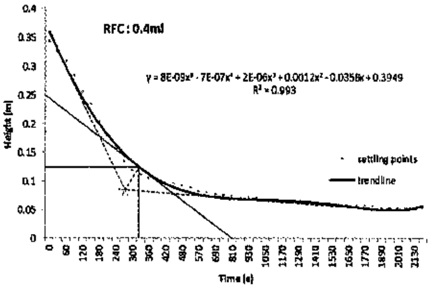
Figure 4-3 (a-f). Settling curves for ferric sulphate 30% concentration as coagulant with varying dosage.


RFC : 0.1ml
y = 7E-09x⁵ - 5E-07x⁴ - 4E-06x³ + 0.0012x² - 0.0361x + 0.39
R² = 0.9932
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

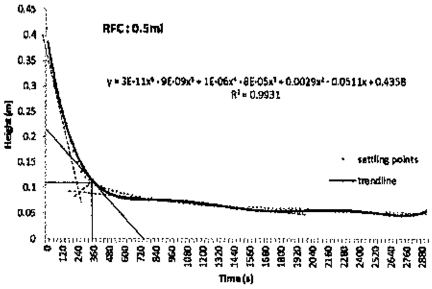
(a)


RFC : 0.2ml
y = 5E-09x⁵ - 3E-07x⁴ - 2E-05x³ + 0.0015x² - 0.0388x + 0.395
R² = 0.9934
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

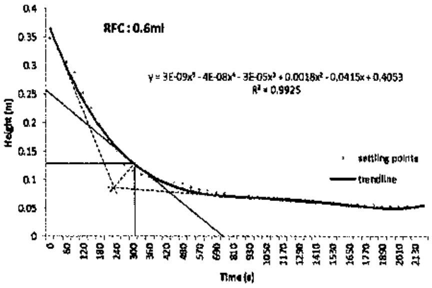
(b)


RFC : 0.4ml
y = 8E-09x⁵ - 7E-07x⁴ + 2E-06x³ + 0.0012x² - 0.0358x + 0.3949
R² = 0.993
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

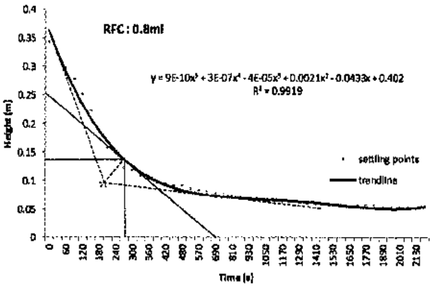
(c)


RFC : 0.5ml
y = 3E-11x⁶ - 9E-09x⁵ + 1E-06x⁴ - 8E-05x³ + 0.0029x² - 0.0511x + 0.4358
R² = 0.9931
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45
Time (s)
0 120 240 360 480 600 720 840 960 1080 1200 1320 1440 1560 1680 1800 1920 2040 2160 2280 2400 2520 2640 2760 2880

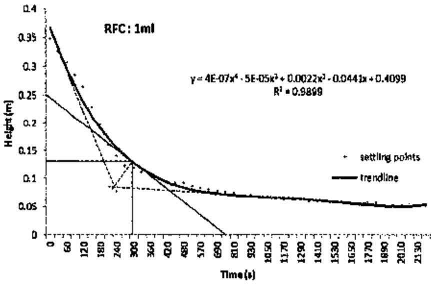
(d)


RFC : 0.6ml
y = 3E-09x⁵ - 4E-08x⁴ - 3E-05x³ + 0.0018x² - 0.0415x + 0.4053
R² = 0.9925
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

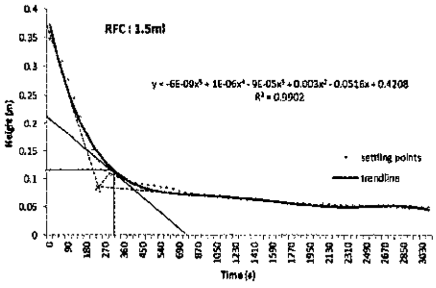
(e)


RFC : 0.8ml
y = 9E-10x⁵ + 3E-07x⁴ - 4E-05x³ + 0.0021x² - 0.0433x + 0.402
R² = 0.9919
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

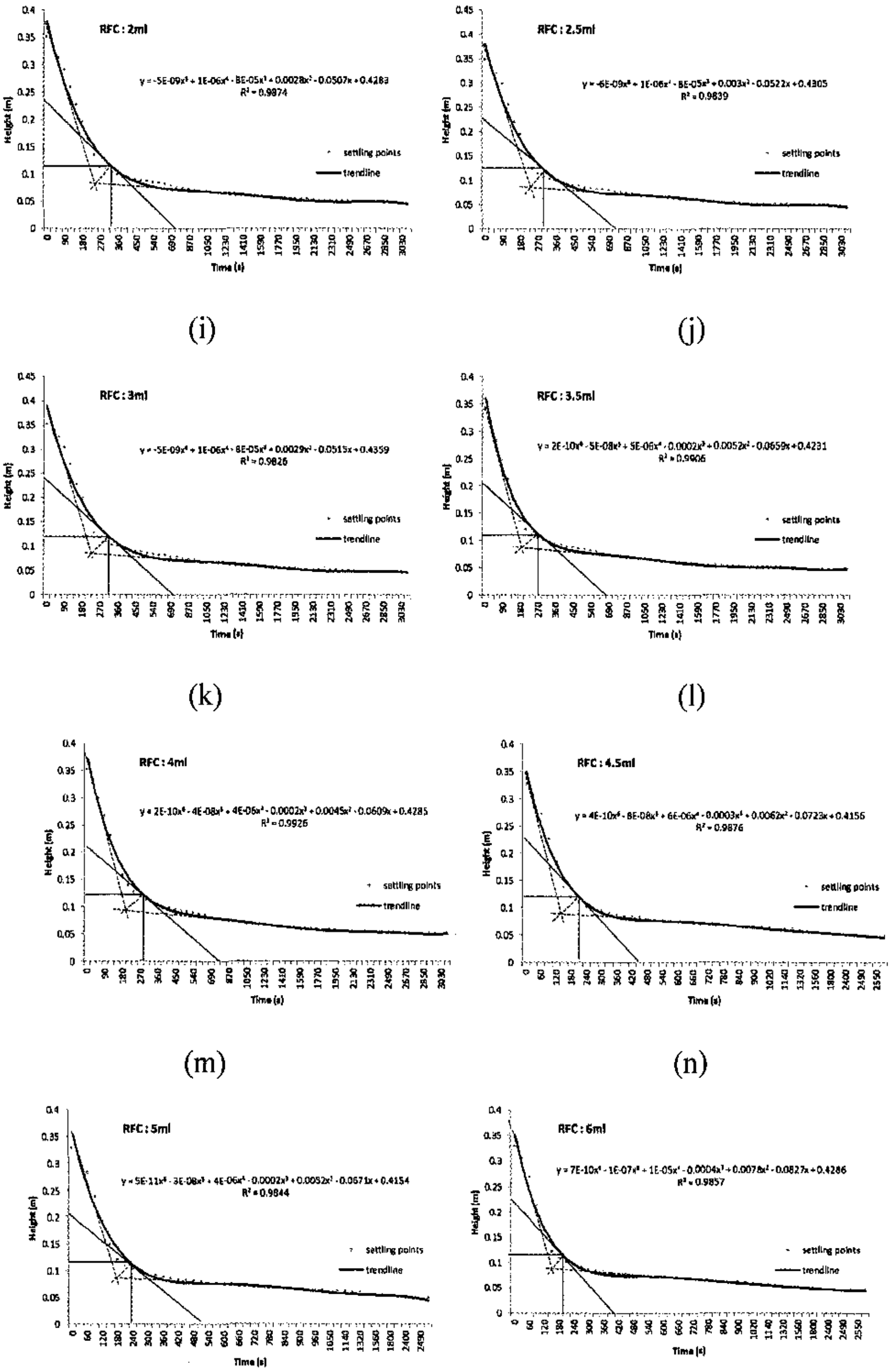
(f)


RFC : 1ml
y = 4E-07x⁴ - 5E-05x³ + 0.0022x² - 0.0441x + 0.4099
R² = 0.9899
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 60 120 180 240 300 360 420 480 570 690 810 930 1050 1170 1290 1410 1530 1650 1770 1890 2010 2130

(g)


RFC : 1.5ml
y = -6E-09x⁵ + 1E-06x⁴ - 9E-05x³ + 0.003x² - 0.0516x + 0.4208
R² = 0.9902
settling points
trendline
Height (m)
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4
Time (s)
0 90 180 270 360 450 540 690 870 1050 1230 1410 1590 1770 1950 2130 2310 2490 2670 2850 3030

(h)



(i) (j)

(k) (l)

(m) (n)

(o) (p)

Figure 4-4 (a-p). Settling curves for Recycled Ferric Chloride as coagulant with varying volume.

The initial height, critical height, and critical time are tabulated in the table below. Settling velocity, v, is computed using the formula

$$v = \frac{initialheight - criticalheight}{criticaltime} \tag{Eq. 4-2}$$

HINDERED SETTLING VELOCITY				
Raw Sample (No coagulant)				
Dosage (mg/L)	Initial height (m)	Critical height (m)	Critical time (s)	Velocity (m/s)
0	0.418	0.09890	330	0.00096697
Ferric Chloride 30%				
Dosage (mg/L)	Initial height (m)	Critical height (m)	Critical time (s)	Velocity (m/s)
60	0.407	0.10247	375	0.00081208
120	0.410	0.10264	365	0.000842082
180	0.410	0.11700	355	0.000825352
240	0.423	0.10908	390	0.000804923
300	0.400	0.12500	320	0.000859375
600	0.404	0.12600	324	0.000858025
900	0.409	0.12600	315	0.000898413
1500	0.400	0.11300	275	0.001043636
2100	0.388	0.10948	285	0.000977263
Alum 30%				
Dosage (mg/L)	Initial height (m)	Critical height (m)	Critical time (s)	Velocity (m/s)
30	0.424	0.11970	420	0.000724286
60	0.480	0.12290	360	0.000991944
120	0.408	0.10000	360	0.000855600
180	0.500	0.11000	420	0.000928600
240	0.450	0.12100	355	0.000926761
300	0.450	0.11290	390	0.000864359

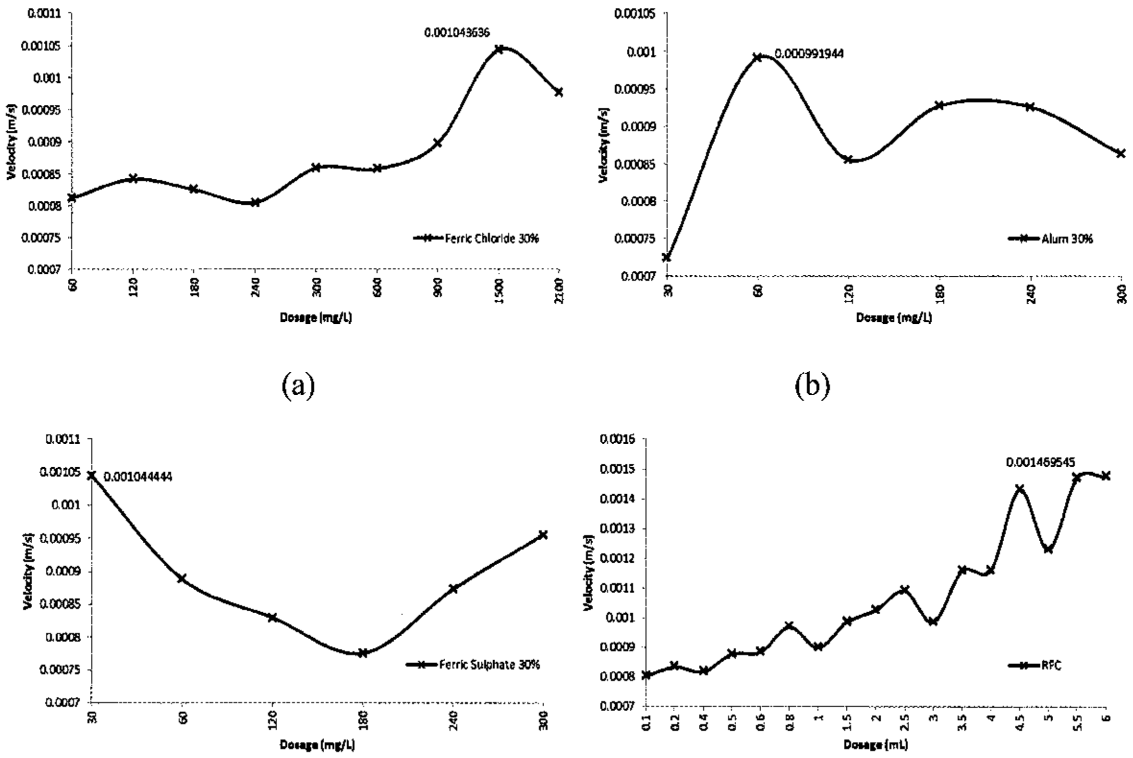
Ferric Sulphate 30%				
Dosage (mg/L)	Initial height (m)	Critical height (m)	Critical time (s)	Velocity (m/s)
30	0.404	0.12200	270	0.00104296
60	0.401	0.13000	305	0.00088852
120	0.384	0.13500	270	0.00092333
180	0.376	0.12000	330	0.00077667
240	0.387	0.12500	300	0.00087400
300	0.383	0.12500	270	0.00095444

Table 4-1. Tabulated data of hindered settling velocity.

HINDERED SETTLING VELOCITY				
Recycled Ferric Chloride				
Volume (ml)	Initial height (m)	Critical height (m)	Critical time (s)	Velocity (m/s)
0.1	0.390	0.12500	330	0.00080303
0.2	0.385	0.11000	330	0.000833333
0.4	0.395	0.12500	330	0.000817879
0.5	0.436	0.12000	360	0.000877222
0.6	0.405	0.14000	300	0.000884333
0.8	0.407	0.14500	270	0.00097037
1	0.410	0.14000	300	0.000899667
1.5	0.421	0.11000	315	0.000986667
2	0.428	0.10500	315	0.001026349
2.5	0.431	0.12500	280	0.001091071
3	0.436	0.12500	315	0.000986984
3.5	0.423	0.11000	270	0.00115963
4	0.429	0.11500	270	0.001161111
4.5	0.416	0.11500	210	0.001431429
5	0.415	0.12000	240	0.001230833
5.5	0.433	0.11000	220	0.001469545
6	0.429	0.11900	210	0.001474286

Table 4-1 (cont). Tabulated data of hindered settling velocity.

Graphs of dosage vs. velocity are plotted to find the optimum dosage of coagulant that has the highest settling velocity.



(a) (b)

(c) (d)

Figure 4-5(a-d). Settling velocity sludge using (a) ferric chloride 30%, (b)alum 30%, (c)ferric sulphate 30% and (d) RFC.

From the graph plotted we can see that the highest settling velocity for ferric chloride is at dosage of 1500mg/L, for alum is at 60mg/L, ferric sulphate is at 30mg/L and RFC is at 5.5mg/L.

4.3 COD AND TSS

Tests for COD and TSS were conducted on all supernatant samples. The results are shown below.

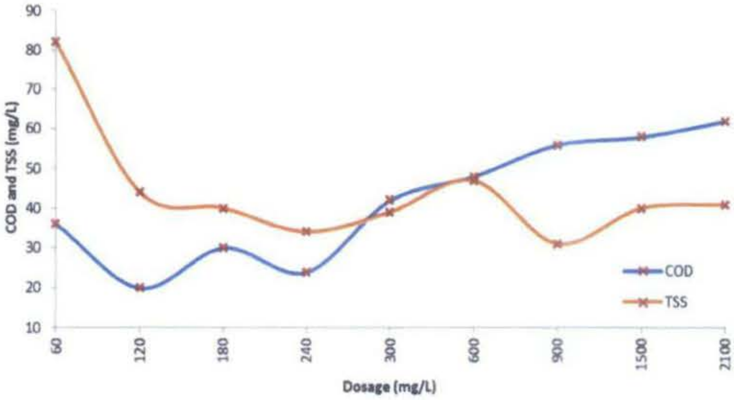


Figure 4-6. COD and TSS curve for Ferric Chloride 30%

Ferric Chloride 30%									
Dosage, mg/L	60	120	180	240	300	600	900	1500	2100
COD	36	20	30	24	42	48	56	58	62
TSS	82	44	40	34	39	47	31	40	41

As shown above, dosage of 240mg/L removed the most COD and dosage of 900mg/L removed the most TSS for coagulant ferric chloride 30%.

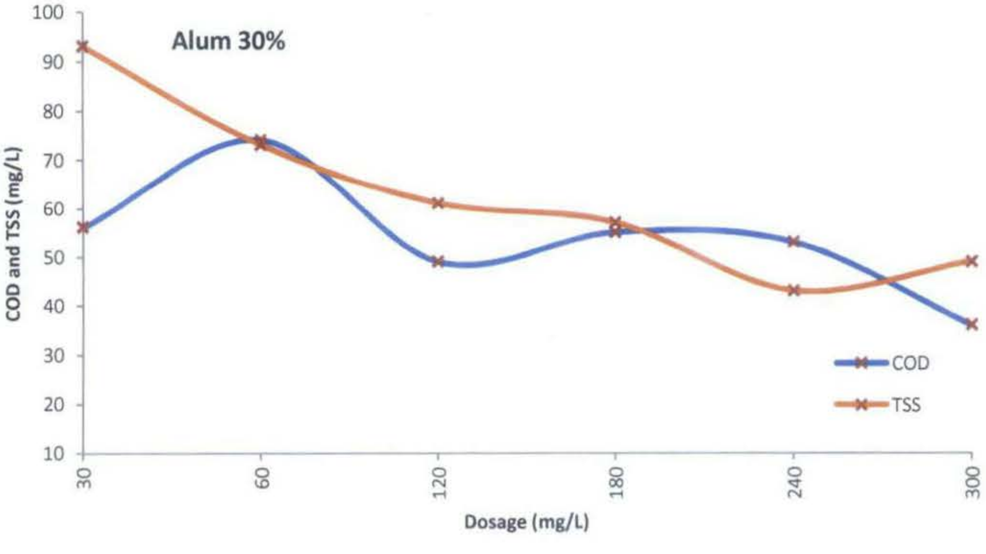


Figure 4-7. COD and TSS curve for alum 30%

Alum 30%						
Dosage, mg/L	30	60	120	180	240	300
COD	56	74	49	55	53	36
TSS	93	73	61	57	43	49

As shown above, dosage of 120mg/L removed the most COD and dosage of 240mg/L removed the most TSS for alum 30%.

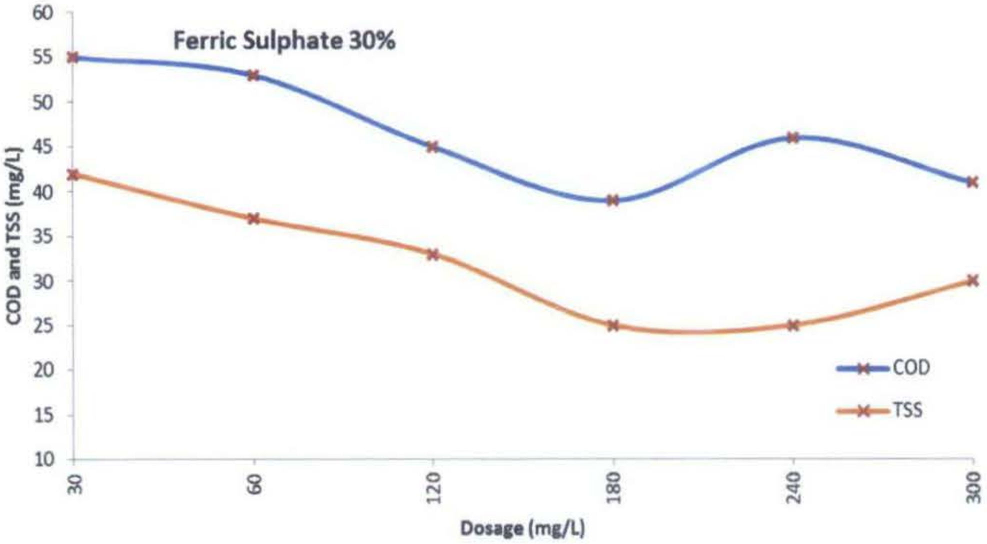


Figure 4-8. COD and TSS curve for ferric sulphate 30%

Ferric Sulphate 30%						
Dosage, mg/L	30	60	120	180	240	300
COD	55	53	45	39	46	41
TSS	42	37	33	25	25	30

As shown above, dosage of 180mg/L removed the most COD and TSS for ferric sulphate 30%.

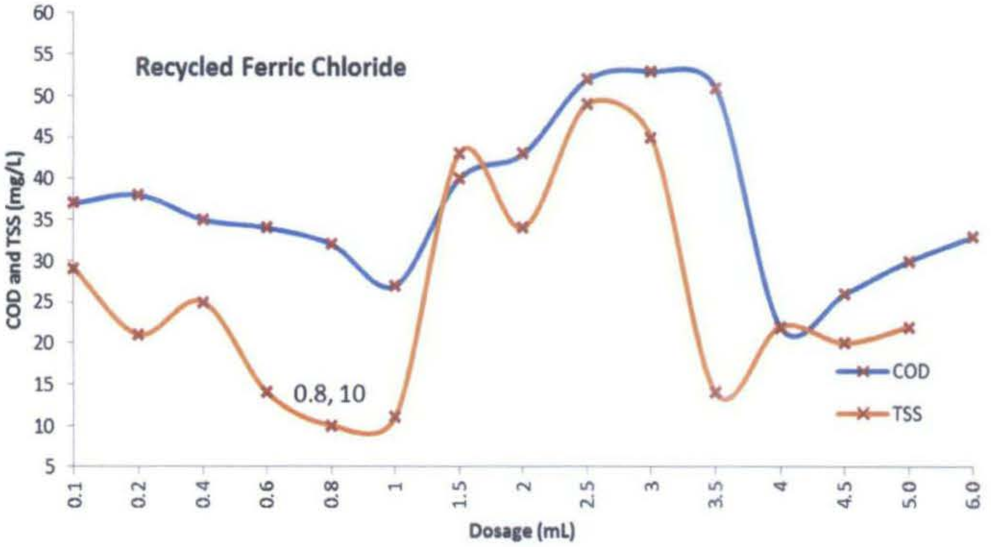


Figure 4-9. COD and TSS curve for RFC 30%

Recycled Ferric Chloride															
Dosage, mg/L	0.1	0.2	0.4	0.6	0.8	1	1.5	2	2.5	3	3.5	4	4.5	5.0	6.0
COD	37	38	35	34	32	27	40	43	52	53	51	22	26	30	33
TSS	29	21	25	14	10	11	43	34	49	45	14	22	20	22	

As shown above, dosage of 1mL removed the most COD and dosage of 0.8 removed the most TSS for RFC.

4.4 CAPILLARY SUCTION TIME

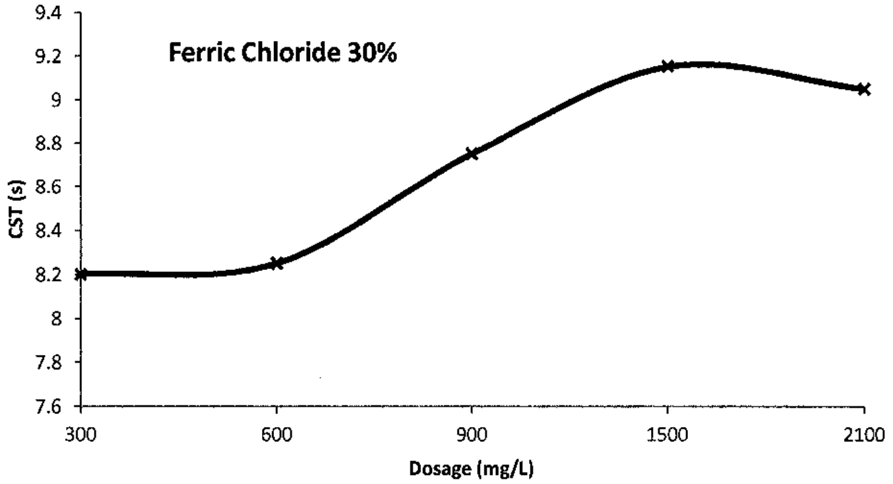


Figure 4-10. CST curve for ferric chloride 30%

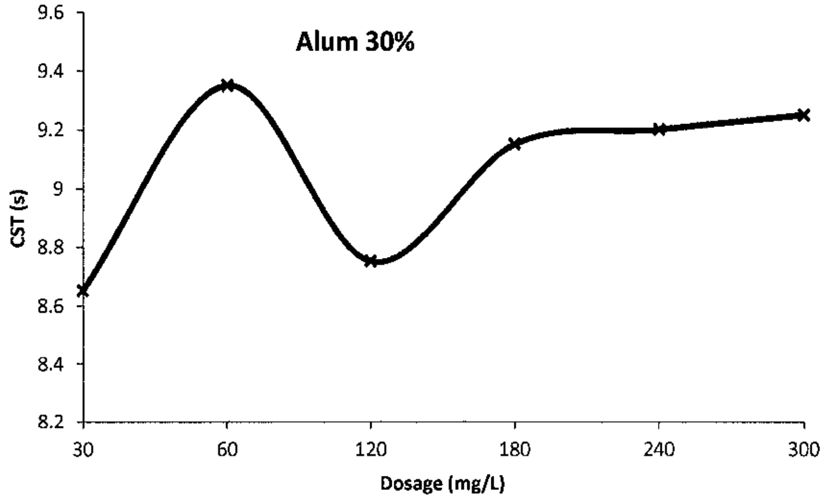


Figure 4-11. CST curve for alum 30%

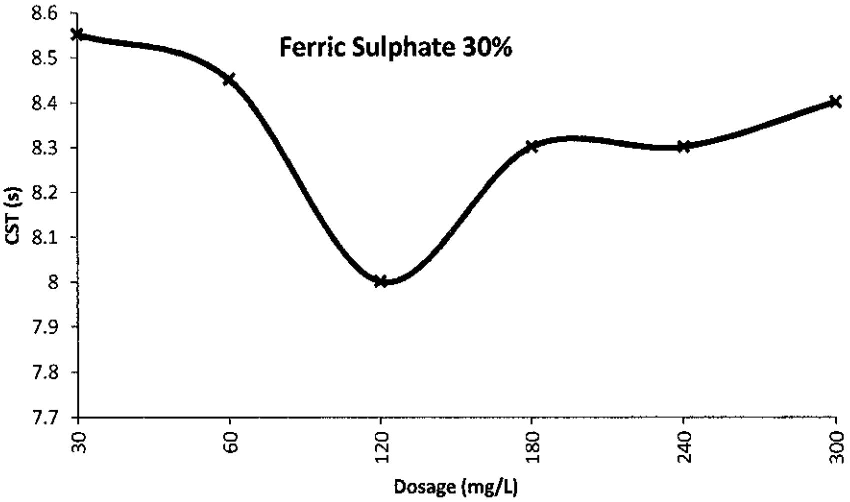


Figure 4-12. CST curve for ferric sulphate 30%

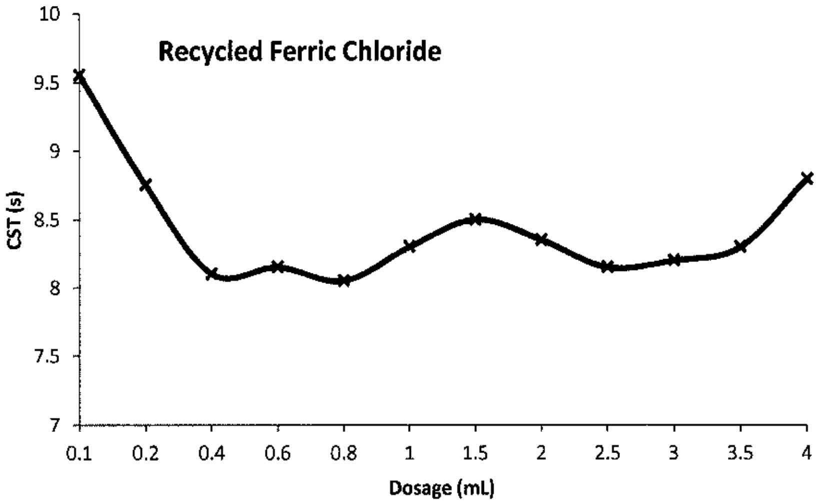


Figure 4-13. CST curve for RFC

Dewatering velocity was measured by dividing the filtration radius with the CST values.

	$FeCl_3$	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	RFC
Max. Velocity, cm/s	0.104	0.099	0.104	0.147
Dosage	1500mg/L	60mg/L	30mg/L	5.5mL

From the result shown it can be concluded that RFC has the highest dewatering rate compared to other coagulants.

4.5 REMOVAL OF COPPER IN SUPERNATANT

RFC was tested for copper concentration. Results showed that the sludge has 922mg/L Cu. Initial copper concentrations of RFC supernatants were obtained. Results are as shown in Figure 4-15. It is found that Cu concentration is lowest with volume of 0.8mL RFC used. 0.8mL RFC also achieved a significantly low COD value of 32mg/L and lowest TSS value of 10mg/L. Thus this volume of RFC is taken as optimum volume. Precipitation method was conducted and the result is as shown in Figure 4-16.

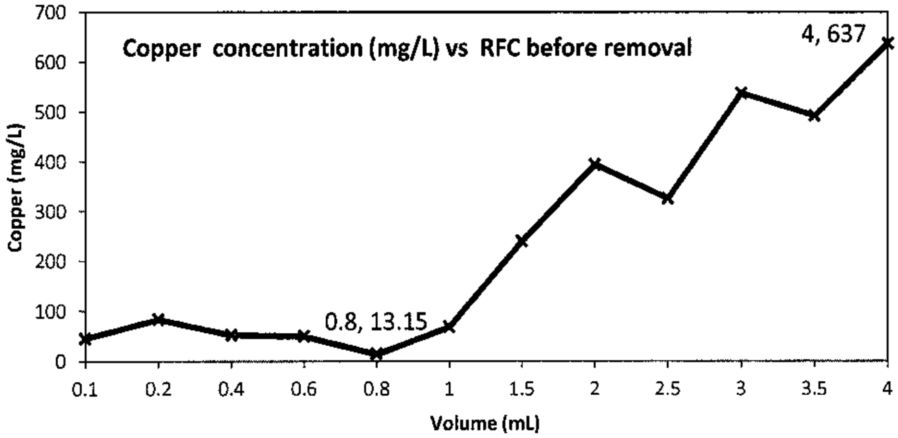


Figure 4-14. Copper concentration in RFC supernatant before pH adjustment.

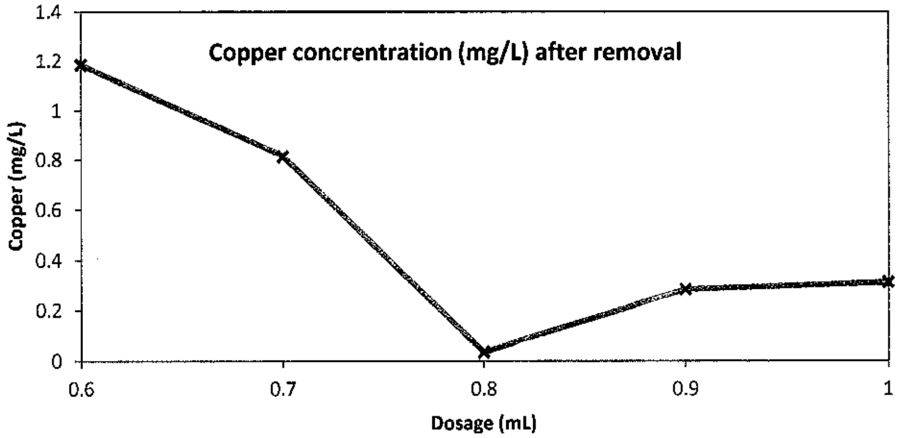


Figure 4-15. Copper concentration in RFC supernatant after pH adjustment.

RFC	Cu concentration, mg/L	Removal efficiency, %
0.8mL without pH adjustment	12.4	99.76
0.8mL after pH adjustment	0.03	

From the results it can be concluded that the removal efficiency of Cu is 99.76%. The Cu concentration value also complies with regulation standard.

Settling velocity was found. Result is as shown in Figure 4.17. CST values were determined and result is as shown in Figure 4-18.

Effluent quality analysis was conducted on the supernatants. Results is as shown in Figure 4-19.

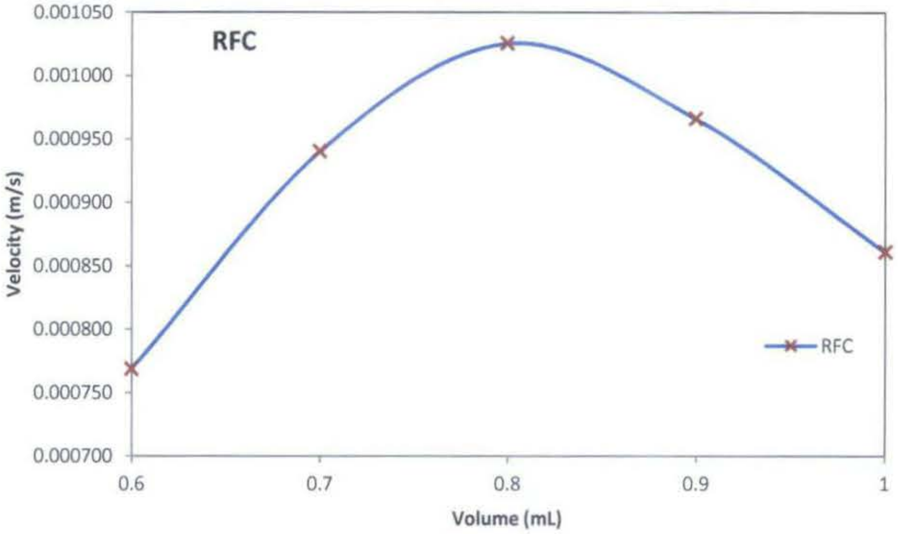


Figure 4-16. Settling velocity RFC supernatant after pH adjustment.

HINDERED SETTLING VELOCITY				
RFC with adjusted pH=9				
Volume, mL	initial height, m	critical height, m	critical time,s	Velocity, m/s
0.8	0.3926	0.0753	270	0.001175
0.6	0.3954	0.0958	390	0.000768
0.7	0.3884	0.0924	315	0.000940
0.8	0.393	0.08553	300	0.001025
0.9	0.4034	0.09921	315	0.000966
1	0.3936	0.1095	330	0.000861

From the result it can be concluded that 0.8mL of RFC generates the highest settling velocity.

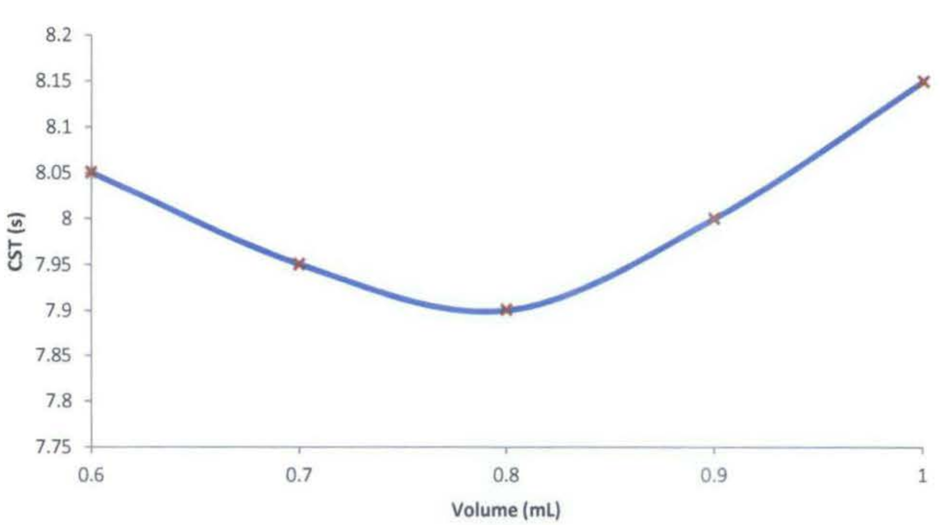


Figure 4-17. CST for RFC supernatant after pH adjustment.

From the graph plotted it can be seen that 0.8mL of RFC yields the lowest CST value hence the best dewatering ability.

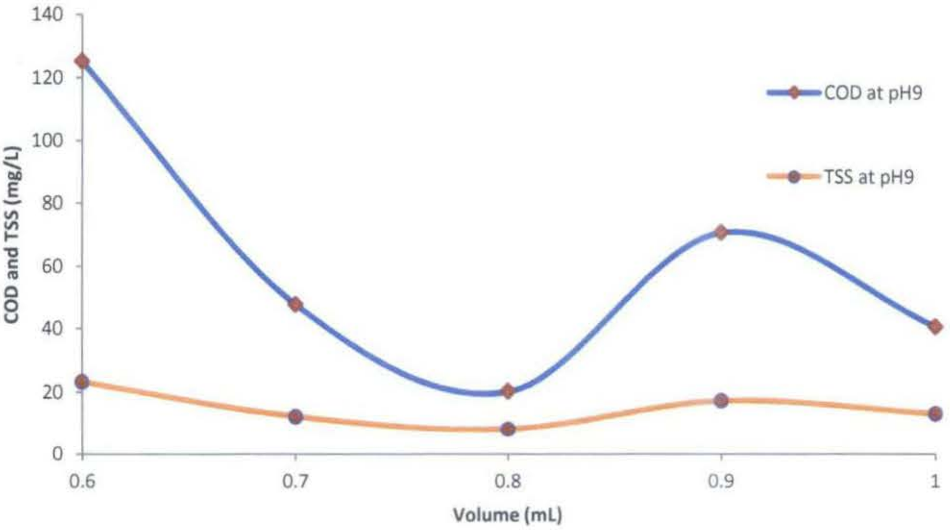


Figure 4-18. COD and TSS for RFC supernatant after pH adjustment.

From the graph plotted it can be seen that RFC volume of 0.8mL generates the lowest COD, and TSS.

CHAPTER 5: CONCLUSIONS

Recycled ferric chloride was used as conditioning agent as replacement of the commercial conditioning agents of ferric chloride, alum, and ferric sulphates. From the result it is seen that RFC has the highest settling rate compared to other conditioners at dosage 5.5mL. COD and TSS value are best obtained from RFC at volume of 0.8mL with COD of 32mg/L and TSS of 10mg/L. RFC flocs with 0.8mL volume also gives the best dewatering rate, followed by ferric chloride, ferric sulphate and alum. From this volume of RFC, copper removal method was conducted and copper was removed with 99.76% efficiency, and yield a CST value of 7.9s.

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