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DEPARTMENT OF CHEMISTRY

CONVERSION OF ALUMINIUM ANODIZING SLUDGE INTO ALUMINIUM POTASSIUM SULPHATE FOR USE AS A COAGULANT IN WASTEWATER TREATMENT

BY

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DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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DEDICATION

To my entire family members especially my parents Gabriel and Ann Riungu; sons Vicky and Leon; sisters Betty, Winny, Late Purry, Kelly, Mercy and Lizz; and brothers Ivin and Twiri.

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ABSTRACT

During the process of aluminium surface treatment, a large quantity of aluminium-rich sludge is generated but its disposal is a great challenge. The main objective of this study was to investigate the potential to recover aluminium from the anodizing sludge for use in. Both wastewater and dumped sludge from various sampling locations in the wastewater treatment plant were characterized. Temperature, pH, total suspended solids, total dissolved solids, turbidity, dissolved oxygen, biological oxygen demand and chemical oxygen demand were analyzed. The final effluent temperature was 28.7±5.8 ^{o}C which was within permitted levels while the pH was 5.8±0.4. The total suspended solids and total dissolved solids were significantly high at 690.6±183.7 and 4,619.8±0.23 mg/l, respectively. The sludge from the dumpsite had solids content ranging from 13.73 % to 16.80 %. Recovery of aluminium from sludges obtained from the dumpsite, wastewater treatment plant and from mixed effluent emanating from process tanks were 87.1%, 77.4% and 64.26%, respectively. Low temperature favoured crystallization of the alum. The alum crystallization yield at 4 ^{o}C and 60 ^{o}C were 92.6 % and 65.3 %, respectively. The prepared alum had higher content of heavy metals especially aluminium and chromium than commercial alum but coagulation performance that compared well with that of the commercial alum. Jar tests gave reduction in wastewater pollution and the optimum settling dosage, pH, temperature and time were 8 g/L, 6.5, 40 ^{o}C and 20 minutes, respectively. These results demonstrate the potential of reducing the pollution posed by anodizing sludge and related wastewater.

Key words: Aluminum anodizing, anodizing sludge, alum, wastewater characterization

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption spectroscopy/ spectrophotometer
APHA	American Public Health Association
BAT	Best Available Technology
BOD	Biochemical oxygen demand
BPT	Best Practical Technology
COD	Chemical Oxygen Demand
DS	Dissolved Solids
DO	Dissolved Oxygen
ECW	Electrical Conductivity of Water
EEA	European Aluminium Association
KEBS	Kenya Bureau of Standards
KEWI	Kenya Water Institute
MACs	Maximum Allowable Concentrations
NEMA	National Environmental Management Authority
NEQS	National Environmental Quality Standards
NTU	Nephelometric Turbidity Units
RPM/rpm	Revolutions Per Minte
SS	Suspended Solids
TS	Total Solids
TSS	Total Suspended Solids
TOC	Total Organic Carbon
UNEP	United Nations Environment Programme

USEPA	United States Environmental Protection Agency
UV	Ultraviolent
WHO	World Health Organization

CHAPTER ONE: INTRODUCTION

1.1 Background of the study

Anodizing is an industrial process which deals with coating metal electrochemically. During aluminium anodizing, the metal is coated under controlled conditions to achieve the required thickness of aluminium oxide (Stepniowski *et al*., 2012). This treatment produces aluminium metal which has longer life with resistance to corrosion and abrasion and also with aesthetic finish. High quality aluminium anodic surfaces are used in architectural building construction, as well as in engineering fabrications. Anodized aluminium finds application in transportation, construction, electrical as well as mechanical equipment (Frie 1972, Xie 2006). This material has unique properties and characteristics which include corrosion resistance, good electrical and thermal conductivity, light weight, workability and ease of recycling (Fan and Kerrich, 1997).

In 1946 an aluminium company in United States of America started work on commercial anodizing (Graves, 2003) and since then, the industry has grown worldwide and very rapidly. These processes however produce large amounts of wastes which include acidic and alkaline aluminium-containing solutions.

During anodizing process, aluminium extrusions are placed on racks and then transported by a crane through the various process treatment tanks and after each treatment some process solution is left on the extrusions. These are then drained and rinsed from the extrusion surface in order to prevent contamination of the succeeding process solution. Therefore, after each process tank, there is a water rinse tank. These rinses are discharged to the waste treatment facility. The alkali waste stream is neutralized with spent anodizing acid and the two are precipitated into aluminium hydroxide which is then allowed to settle. One of the major challenges encountered by anodizing plants is the disposal of the large amount of sludge produced. The cost of disposal which mainly includes transportation cost is very high. Usually the sludges are dumped on a land fill in the plant site where they still pose the environmental problems. The process also generates large amounts of liquid effluents which ideally must be treated to meet the discharge limits specified by the local authorities before being discharged into sewer systems. This has made the recycling of anodizing of great importance to both anodizing industries and the environmental regulatory agencies.

Large amounts of sludge is generated at the wastewater treatment plant when separating solids from aqueous solutions. Aluminium hydroxide is brought into liquid solution during the degreasing and etching stages (Patel, 2008) and Al is removed or dragged out from the reaction tanks to the rinsing stages. Therefore, rinses after etching and anodizing are the main source of pollution for effluent generated from the anodizing plant (Metcalf and Eddy, 2003). This drag out is taken positively by some operators since it helps in the maintenance of the etching solution concentration and its life elongation. To stabilize sodium aluminates in etching baths, complexing agents are usually added to maintain solution viscosity and to ensure it sticks to the extrusion surface, thus increasing the quantity of caustic soda dragged out

In some anodizing plants, this sodium hydroxide is regenerated by continuous recirculation of the etch solution between the etching tank and a crystallizer. This technique is in use in European countries like Switzerland, France and American (Teseliboi, 2010). Alternatively, the aluminum metal which is the major component of the precipitated sludge can be extracted from the sludge by adding stoichiometric quantities of sulphuric acid followed by crystallization using potassium sulphate as shown in the following equations.

$$2Al\left(OH\right)_{3(aq)} + 3H_2SO_{4(aq)} \rightarrow Al\left(SO_4\right)_{3(aq)} + 6H_2O$$

1.1

$$K_2SO_{4(aq)} + Al\left(SO_4\right)_{3(aq)} \rightarrow 2KAl(SO_4)_{(s)}$$

1.2

This is a rapid and exothermic process which is completed at a temperature of 50 ^{o}C to 100 ^{o}C in 60 minutes (Patel, 2008). The product is liquid alum which is then crystallized. The solid product is widely used in flocculation of colloidal matter during water treatment.

1.2 Statement of the Problem

During the process of surface treatment of aluminum and its alloys, large quantity of waste is generated. Most of these wastes are discharged into sewers or water bodies without adequate treatment to remove the metals. The disposal of anodizing sludge and wastewater is a great challenge to anodizing industries due to their complex nature. The high cost of disposing these wastes and their environmental impacts necessates development of methods for waste minimization. One alternative involves putting the sludge to various uses; it can be treated and modified to become alum, i.e. potassium aluminum sulphate for use in wastewater treatment. The alum can then be sold to other wastewater treatment plants. Solutions such as sodium hydroxide used in the etching tank can also be regenerated and re-used. This would result in less amount of acid required to neutralize the alkali rinse water.

The goal of this study was to recover aluminum from an anodizing sludge to make alum for wastewater treatment. The source of the sludge was an aluminum anodizing company located in Thika Municipality, Kiambu County, Kenya. The plant generates significant quantities of effluents and sludge which require to be treated to comply with the local authorities' effluent discharge limits to the sewer system. Before making the alum, it is important to determine the characteristics of both the liquid effluents and the sludge. Making a useful product out of the waste would benefit the company by reducing cost of disposal as well as ensuring compliance with requirements of the local environmental authorities.

1.3 Objectives

1.3.1 Overall objective

To reduce the environmental pollution of anodizing plants through recovery of aluminium from anodizing sludge in the form of potassium aluminium sulphate.

1.3.2 Specific objectives

1) To determine physicochemical wastewater effluent from a local anodizing plant.
2) To characterize the sludge from the anodizing plant
3) To prepare alum from the anodizing sludge
4) To determine the performance of prepared alum as a coagulating and flocculating agent for wastewater.

1.4 Justification

Aluminium anodizing process involves aluminium off the metal and the use of many chemicals some of release heavy metals into the wastewater. The physical appearance of effluents emanating from local anodizing plants indicates lack of compliance to discharge standards and actual environmental pollution. Waste management methods currently being used by local anodizing industries result in accumulation of solid sludge in dumpsites which hence contribute to land and ground water pollution. These two aspects point to an existing waste disposal problem that need addressing. A better sludge management solution will not only reduce environmental pollution but will also increase the competitive edge of local aluminium anodizing companies. To achieve this goal, physical characterization of the liquid effluent and the solid sludge is necessary as a basis for improvement of the waste management process.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Manufacturing industry is important to any economy since it contributes to a country's economic growth as well as creation of jobs. However industrial activities have a significant impact on the environment due to different categories of waste produced. Industrial ecology aims at zero-waste which is not always achievable, being the long term solution to sustainability (Teseliboi, 2010). Zero waste ecology encourages recycling of resources so that all waste substances are re-used and minimal residues are sent to landfill. The process works similarly to the way nature works in managing and reuse of its resource (Wernick and Graedel, 2002). It involves creating commodities out of the waste products by converting waste products into raw materials for other industrial sectors. The zero waste idea therefore helps in creating a hierarchy with order of preference and importance, recycling, treatment, reuse, prevention and finally disposing (Vincent e*t al.*, 1999).

Aluminium anodizing involves a series of processes that change the surface of manufactured items to get specific properties. The main role of surface finishing is to improve the appearance, reflectivity, corrosion and wear resistance and hardness of the products. It modifies their electrical conductivity, remove blurs and flaws and finally control surface friction (Dotzer *et al.*, 1976). Anodized aluminum is used in electrical, automobile, aerospace, building construction, food and beverage industries as well as in the manufacture of containers and industrial equipment (Teseliboi, 2010).

The most undesired results of industrial activity are production of hazardous solid waste and liquid effluent which end up causing land and water pollution and emission of gaseous waste into the atmosphere. Heavy metals rank first among the most dangerous waste pollutants discharged by anodizing processes (Amigo, 2001).

2.2 The purpose of aluminum anodizing

There are varied reasons why aluminum should be anodized, including to remove contamination from the aluminium metal surface (Sheasby and Pinner, 2001). According to others include:

i. Removal or reduction of flaws in order to provide a uniform physicochemical and electrical behavior of the aluminium surface
ii. Removal of any geometrical defects on the aluminium bar
iii. Modifying appearance by making the surface either dull or bright depending on the need
iv. Making the surface corrosion resistance properties
v. Giving the surface a specific aesthetic effect
vi. Allowing dyeing or coloring of surface
vii. Improving lubrication and adhesion.

2.3 Process operations

The word anodizing is used for the process since the component to be treated is made the anode, the positive pole of an electrochemical cell. Anodizing can therefore be defined as an electrolytic process which is used to add a layer made of oxide on the surface of aluminium or metal parts being treated (Corriea *et al.*, 2005).

The process takes place in very well-defined stages starting with degreasing in organic solvents, and this is followed by etching treatment in an alkaline solution. Appropriate rinsing schedules are used to remove residual solution and this also limits cross contamination with the succeeding solutions. Electrochemical processes such as alkaline etching leave a residual film on the aluminium surface hence desmutting in nitric acid is done to remove contaminants on aluminium film developed during alkali degreasing. Immersion in nitric acid solution also removes some residual metal impurity. With the knowledge of the factors which control film growth, composition and morphology, well defined aluminium films can be produced in suitable electrolytes for different applications (Patel *et al*., 2004).

One such resistance to atmospheric corrosion and erosion. It is also easy to impregnate anodic film with organic and inorganic pigments to produce decorative articles. Another well-known and successful application of anodized aluminium application of aluminium anodizing is to produce anodic films which are used for architectural applications (Patel *et al*., 2004). The porous material is filled by sealing to develop films of thickness of about 25um which provide is in aerospace. This involves anodizing in chromic acid followed by top coating (Lisbona *et al*., 2012).

2.4 Typical anodizing process

Generally, aluminium anodizing process occurs in well-defined stages which include pretreatment, etching, anodizing, coloring and sealing. This process is shown schematically in Fig. 2.1.

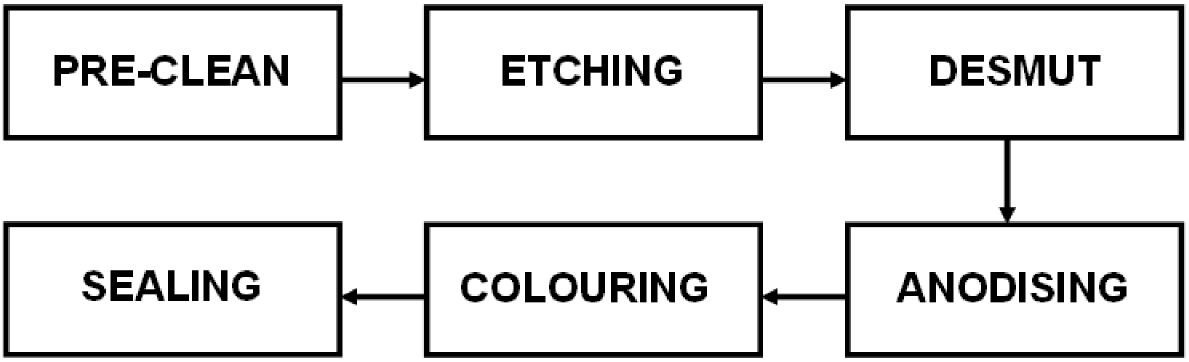

Figure 2.1: Anodizing process flow diagram (Patel, 2008)

After each stage the components are dipped in rinse tanks to prevent contamination of next process solution. Wastewater from the rinse tanks is discharged to the wastewater treatment plant for treatment before final discharge. Apart from the treated wastewater, anodizing produces a sludge which causes disposal problems. Details of anodizing process are outlined below. Patel (2008) has given operating conditions of the various operations in a typical anodizing process.

2.4.1 Pre-treatment

The use of trichloroethylene vapor in degreasing is covered by very stringent regulations (Graves, 2003) and hence has been replaced by alkaline degreasers. These are based on mixtures of soda, tri-sodium phosphate and sodium carbonate (Andreazza and Langlade, 2001) to remove grease or lubricants from aluminium surface. During this process, a small amount of aluminium is dissolved thus leaving a clean etched surface. Some inhibitors are often used to prevent excessive etching of the aluminium. In some cases, acid cleaners have been used.

2.4.2 The Etching Process

This can be done using either alkaline etch formulations or acidic etch formulations. A typical alkaline etch formulation consists of sodium hydroxide, mixed with sequestering agents as well as surfactants. Usually, there is buildup of aluminium precipitates in the etch solution. An equilibrium may be reached where quantity of metal removed by etch solution is equal to the amount of metal removed by drag out effect (Strazzi and Belle, 2002). Drag out, also referred to as dumping, is done continuously into the rinse solution.

Acidic etching is done using concentrated acids at 100 ^{o}C and results in production of a high degree of specularity on the part being anodized. The acidic solution also removes aluminium which is carried away by rinse water (Tariq *et al.*, 2006). The prolonged etching produces a satin or matt finish which can be used for nameplates or decorative architectural work as well as deep engraving and chemical milling (Graves, 2003).

During alkaline etching, aluminium dissolves in caustic soda producing hydrogen gas and forming sodium aluminates which exists in alkaline state. The chemical reaction of this process is shown in equation 2.1 below:

$$2Al_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow 2NaAlO_{2\,(aq)} + 3H_{2\,(g)}$$

(2.1)

The unreacted caustic soda decreases as the reaction proceeds resulting in a drop of etching rate and electrical conductivity of the solution while viscosity of solution increases (Misiole, 1996). The reaction becomes very slow and eventually the clear or sometimes a brownish solution turns to milky white. Typically, when the concentration of free caustic soda drops to about 25% of the total caustic concentration, the sodium aluminates will hydrolyze releasing free caustic soda and hydrated alumina or aluminium hydroxide precipitate as shown in equation 2.2 below:

$$NaAlO_{2(aq)} + 2H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$$

(2.2)

At this point etching suddenly increases because free caustic soda is now available for continued etching. Caustic soda solution in continuous use takes aluminium into solution until the uncombined caustic soda is approximately one quarter of the original total soda. The hydrate slowly settles onto the tank bottom and sides, and then dehydrates into alumina which is a very hard rock, and very difficult to remove. The reaction is shown in Equation 2.3.

$$2Al(OH)_{3(aq)} \rightarrow Al_2O_{3(s)} + 3H2O_{(l)}$$

(2.3)

Therefore, the etching tank is responsible for the formation of most solid wastes which contain mainly aluminium compounds. Usually complexing agents are added to the etch tank to prevent precipitation of aluminium hydroxide and the hard rock (Wukasch and Dalton, 1993).

2.4.3 Anodizing

Electrochemical anodizing process is done in an acidic electrolyte made of acids such as sulphuric acid, phosphoric acid or chromic acid (Furnea and Finlayson, 1996). Aluminium ions dissolve in the electrolyte and its concentration is controlled to a maximum level. Some aluminium is removed through drag out into post rinse solution.

The dissolved aluminium can also be removed by periodic dumping or regular bleed off into effluent treatment system.

2.4.4 Colouring

Colouring of anodized components is done using three major ways which include integral color anodizing, pigmentation with organic and inorganic dyes, or electrolytic pigmentation in metal salt solution (Stepniowski *et al*., 2012). In electrolytic coloring, aluminium solutions of copper, cobalt, nickel and tin salts are used. The main consumption of chemicals in these electrolytes is by drag out into the post rinse and the effect of this is coloration of the water. The tin and cobalt electrolytes are neutralized and the metals are removed in the effluent treatment system. The dye solutions used are normally operated at 60^oC. This leads to use of a static rinse after dye solution from which the dye is removed by a carbon filter on a closed loop system Metcalf and Eddy, 2003.

2.4.5 Sealing

Sealing can also be called hard walling. Distilled water at 96 ^oC and pH 6.0 is used for a period of 2-3 min. The solution contains ammonium acetate or nickel acetate together with anti-smut additive which contain glucose or dextrose. The solution becomes contaminated with sulphate and aluminium ions. Aluminium precipitates as aluminum hydroxide, though this has no effect on sealing. Sulfates, silicates or fluorides affect the process by inhibiting the sealing process and reducing sealing efficiency. Nickel and cobalt are very suitable for reducing losses of color after dyeing. This sealing can also use nickel fluoride in cold impregnation process (Metcalf and Eddy, 2003). The post rinse is static hot water. The large amounts of nickel found in the wastewater come from the sealing stage.

2.5 Process waste solution

The effluents are derived from the main stages above namely pre-clean, etching, desmut, anodizing and seal stages. There are two major waste streams; spent anodizing acid and alkaline wastewater solutions. Ideally, the acid rinse is separated from alkaline rinse water until the two are mixed in the effluent treatment tank. This minimizes excessive use of fresh acid or alkaline in pH adjustments and see sawing of the pH in the mixing effluent treatment tank. (Stepniowski *et al.*, 2012).

During the anodizing process, many different stages of rinsing are involved since there is always some drag out from the chemical process solution into the rinse solutions. Most contaminants in the rinse solutions are usually precipitated when they are neutralized, while others, for example sodium and sulfate ions remain in the solution. But sulfate ions can be reduced to about 2,000 mg/L by neutralization with lime, otherwise ion exchange or barium ions are required (Kirman and Korach, 1991).

2.5.1 Precipitation

The neutralization of rinse water is usually followed by precipitation and consolidation of metal hydroxide. Rinse water is then treated with a flocculating agent to help in precipitation and settling in a designed settling tank (Gregory and Duan, 2001). Treated water flows from the top of this settling tank to a final tank for pH checking and adjustment before discharge to the municipal sewer or water course. The sludge is then taken from the bottom of settling tank for further consolidation.

2.5.2Precipitation chamber (PC)

Patel (2008) describes a precipitation chamber in a New Zealand anodizing plant. The wastewater after neutralizing using sulphuric acid is thoroughly stirred and the pH adjusted using 50% w/w caustic soda solution. After this alkali treatment stage, wastewater overflows into the flocculation chamber by gravity. The polyelectrolyte is added to encourage flocculation of the precipitate. After clarification, the solids-free clear supernatant effluent flows from the top of the clarifier and the settled sludge is taken to a settled solid tank.

2.5.3 Sludge consolidation

The volume of the sludge is greatly reduced by either optimizing the settling process through some dewatering technologies. There are several techniques available for sludge dewatering which include rotary vacuum filtration, filter pressing and centrifugation but the most common method is the filter press which gives the driest cake with 20-30% solid. It also has lower capital, operating and maintenance cost, low noise, small space requirement and low tendency towards leakage. However, it has the disadvantages of short life of filter cloths and batch operation mode (Noyes, 1993).

2.5.4Waste rinse water solutions

In the process operation, the parts to be anodized are placed on a rack and a conveyor then passed them through several stages. Some process solutions usually remain on the pieces being treated, and to prevent contamination by this carry over, a water rinse is done between each process stage. This rinse water gets contaminated leading to a buildup of the ions, which include aluminium being the main one, and others like Cr, Fe, Si, Mg, Cu and Zn in the rinse solutions (Yuan *et al*., 2001). This solution is usually dumped, but sometimes it is replenished with active ingredients and finally, bulk dumping is done. Use of long life etch chemical additives, continuous dumping by drag out and continuous bleed off are some of the methods used to control level of contaminants in respective solutions (Panswad and Charmnan, 1992).

2.5 Anodizing sludge utilization options

The common practice in handling of anodizing sludge is mainly by land fill disposal which has its associated environmental problems. Patel (2008) describes anodizing sludge problem in a New Zealand plant which was producing 12 tonnes of sludge per week. In developed countries, the anodizing waste has been put into various uses. These uses include addition in ceramic bodies (Ribeiro *et al.,* 2002), synthesis of pigments along with kaolin and clay (de Oliveiral *et al*., 2003), production of mullite-aluminium refractory ceramics (Tulyaganov *et al.*, 2002), treatment of paint industry wastewater and treatment of municipal water, (Correia *et al*., 2005)

Most third world countries are yet to find ways of utilizing this anodic solid. Current practice is to reduce it, treat the effluent and dump the sludge in a dumpsite.

2.6 Wastewater Coagulation

Patel (2008) has reviewed the subject of coagulation, the process that brings about aggregation of small particles that are suspended in liquid media, thus reducing turbidity. Since the particles are mostly negatively charged, coagulants such aluminium sulphate, aluminium chloride and sodium aluminates act by neutralizing the charge and the floc formed when particles aggregate trap impurities (Bratby, 2006). The aluminium based coagulants including polymerized forms have good floc formation and low sludge volume.

Alum or potassium aluminium sulfate is used in wastewater treatment. It works through the coagulation process and provides a very high efficiency removal of different parameters, which include COD, BOD, suspended solids, turbidity, color and micro-organisms. These are removed from their colloidal suspensions. The chemical, potassium aluminium sulphate has been in use since ancient times when Egyptians used it to reduce cloudiness in water (Bartolomeu *et al*., 2005). The process of coagulation-flocculation is made up of three consecutive steps; coagulation of suspended solids, growing of micro-floc and elimination of the floc aggregates formed, (Melia and Amiritharajah, 1990). The process is strongly influenced by wastewater composition together with other kinetic process parameters which include rapid and slow stirring and mixing steps. The initial phase of coagulation occurs with rapid mixing. The coagulating species cause destabilization of flocs which are carried by turbulent eddies interacting with the solids in the solution by collisions. The rapid mixing step is then followed by the second phase where less intense agitation and floc growth takes place up to sizes suitable for removal. This is followed by settling. Alum made from anodizing plant can be used to coagulate suspended solids in wastewaters from the same plant (Metcalf and Eddy, 2003).

Turbidity measurements represent a convenient experimental procedure for the determination of the stability of colloidal suspensions. As aggregation occurs and colloids settle out of solution, turbidity decreases. Coagulation and flocculation process is strongly influenced by other factors such as kinetic parameters, temperature, time of slow/rapid mixing steps and the energy input during different phases, (Renault *et al*., 2009). Therefore, it is necessary to try and establish the influence of some of these factors such as temperature and time for different combinations of coagulant dose.

2.6.1 Theory of coagulation

Colloidal systems exhibit turbidity since they scatter light, and this is related to the sizes of the particles involved. These particles in the systems have negative electric charges on their surface which cause repulsion on each other, preventing them from colliding to form large masses called flocs and settling. Chemicals are added to the wastewater to promote destabilization of negatively charged particles thus causing coagulation and aggregation or flocculation of suspended solids into particles large enough to settle or be removed (Eastland and Wright, 1999).

The major inorganic coagulants include aluminium sulfate and iron chloride which have a low solubility. Since water has hydroxyl ion (OH^-), it reacts with the respective metal ions forming iron hydroxide and aluminium hydroxide precipitates. Other hydrolysis products formed include, $Fe_2(OH)_3$, $Al_2(OH)_3$, $Fe(OH)^{2+}$, $Al(OH)^{2+}$, $Fe(OH)_4^-$, $Al(OH)_4^-$ (Hammer, 1986). The pH, temperature and hydrolysis product influence the predominant coagulation mechanism as observed by Gregory and Duan (2001).

Organic polymers can also be used as primary coagulant in binding already formed small flocs into lager particles in water and industrial effluents treatment. A major use of organic polymers is as a coagulant aid in bridging the coagulated particles formed when aluminium or iron salts have been used as primary coagulants. The large aggregates formed then settle more rapidly (Barton, 1991).

A new source of natural coagulant and flocculating agent are tannins. A study conducted by Beltran and Sanchez (2009) used an agent called TANFLOC, a tannin based coagulant and flocculants for treating urban wastewater. Another tannin based product was obtained by Ozacar and Sengi (2000) from valonia tree from Turkey. These workers demonstrated that tannin has a very good effect when combined with aluminium sulfate for the purpose of enhancing further stages of sludge removal (Heredia and Martin, 2009). Correia *et al*. (2005) studied the use of aluminium anodizing waste as a coagulant for the treatment of wastewater.

2.7 Aluminium recovery from the sludge

Extraction of alum from ashed anodizing sludge and its crystallization can be done as per the following equations below (Pansward and Charmnan, 1992).

$$2Al_{(s)} + 2KOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2K[Al(OH)_4]_{(aq)} + 3H_{2(g)}$$

(2.4)

$$2Al_{(s)} + 2KOH_{(aq)} + 4H_2SO4_{(aq)} + 22H_2O_{(l)} \rightarrow 2KAl\,(SO_4)_2.12H_2O_{(aq)} + 3H_{2(g)}$$

(2.5)

$$2Al(OH)_{3(s)} + 3H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 6H_2O_{(l)}$$

(2.6)

$$Al_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + 24H_2O_{(l)} \rightarrow 2KAl\,(SO_4)_2.12H_2O_{(aq)}$$

(2.7)

The overall equations for the process become:

$$2Al_{(s)} + 2KOH_{(aq)} + 4H_2SO4_{(aq)} + 22H_2O_{(l)} \rightarrow 2KAl\,(SO_4)_2.12H_2O_{(aq)} + 3H_{2(g)}$$

(2.8)

The equations for the extraction and crystallization process are equation 2.6 and 2.7, given above.

In order to extract available aluminum, the equations are used to establish the quantity of sulphuric acid required to complete the extraction process. According to Saunders *et al*., (1980) aluminum anodizing sludge is made up of three major components: aluminium as aluminium oxide and hydroxide, water and trace quantities of metals, dissolved salts and other contaminants. The equations for extraction and crystallization process are equation 2.6 and 2.7.

From the equation and simplification described above, the acid requirement for the extraction of aluminium from the sludge cake is 1.89g sulphuric acid per g of aluminium hydroxide. Saunders *et al* (1980) showed that the aluminium content of the fixed solids in aluminium anodizing sludge cake varied from 32.4% to 39.7%. The theoretical value of aluminium content in $Al(OH)_3$ is 34.6%. This can be used to calculate amount of aluminium in the sludge and sulphuric acid required as well as amount of potassium sulphate needed in the process.

In these calculations it is assumed that the additional loss in mass following exposure to 105 ^oC in the analysis for fixed solids is indicative of the volatile matter in the sludge and loss of bound moisture associated with gelatinous aluminium hydroxide precipitates.

2.8 Scope of work

This work is therefore meant to improve knowledge on use of aluminium anodizing sludge especially in wastewater treatment. The sludge and wastewater used are from a local aluminium anodizing industry within the metal surface treatment sector. Using this sludge has several economical, technical and environmental advantages which include, cost saving because of decreased production of solid waste in the industrial process, reduced usage of reagent and treatment process. This means a decrease in handling, transport and disposal of waste and monetary income from commercialization of sludge alum produced from waste.

Other advantages are decreased impact of the anodizing process on land due to reduction of solid waste dumping. The environmental impacts of aluminium hydroxide produced by the process will be reduce through reuse and recycling.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Introduction

The leading aluminium extrusion company in Kenya is located in Thika Municipality in Kiambu County. Thika town is 40km North of Nairobi city and lies between 1^0 3'S and 37^0 5'E at an altitude of 1500m (KNBS, 1994).

3.2 Materials and equipment

The chemicals used were: 2M analytical grade nitric acid usually 69% HNO_3, 2M analytical grade sulphuric acid, 2M analytical grade hydrochloric acid, distilled deionied water and kaolin. Atomic absorption spectrophotometer (SHIMADZU Model AA-6300) was used for heavy metal analysis. The other instruments were from Kenya Water Institute laboratories and they included pH meter (HI8014 Hannah Instruments), mercury thermometer, DO oximeter, a conductivity meter for measuring dissolved solids, KNF NeurbergerLaboport for measuring TSS, hot plate/stirrer, turbidity meter, laboratory hot air oven, BODOXiTop Box from WTW and a jar test apparatus (Flocculator SW6) from Stuart.

3.3 Wastewater sample collection and preservation

Wastewater used in this study was collected in sealable plastic containers which were first cleaned, dried, pre-rinsed with the waste solution before putting samples in them. The samples were collected from five different sampling points at the anodizing plant: rinse feed water (Sample A), anodizing tank rinse water discharge (Sample B), etching tank rinse water discharge (Sample C) and final effluent entering the treatment plant (Sample D). The sampling was done three times on different dates i.e. on 4th April, 18th April and 23rd May 2013. Sample temperature and pH were measured within two hours at the sampling site. Samples were preserved as shown in Table 3.1 prior to analysis for the respective parameters.

Table 3.1: Sample preservation methods

Parameter	**Preservation method**
BOD	Samples stored in a fridge at 4^oC and preserved for 48 hours.
COD	Sulfuric acid was added to preserve sample for 28 days.
Metals	Nitric acid was added to preserve sample for 6 months.

3.4 Anodizing sludge sampling and preservation

The sludge was collected from three locations at: the bottom of the etching tank, the waste treatment plant inflow and approved dump site (See Figures 3.1 and 3.2). Material drawn from each location was mixed using a stirring rod to obtain a representative sample. Dry sludge samples such as those obtained from the dumpsite were stored in plastic bags while wet ones, such as those from the bottom of the etching tank were collected in dry plastic containers.

Figure 3.1: Sludge deposit next in the vicinity of the wastewater treatment plant

Figure 3.2: Solid aluminium sludge at the dumping site

3.5 Determination of physiochemical parameter of wastewater.

Wastewater samples were analyzed for various parameters, which included pH, temperature, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), dissolved solids (DS), turbidity, sedimentation rate (rate of settling) and metal ion content. Analytical techniques employed in this study were based on the standard methods for examination of water, wastewater and environmental monitoring (Cresceri, 2005)

3.5.1 Determination of pH

The pH was measured using a pH meter HI8014 Hannah Instruments. The pH meter was calibrated using a standard solution (Cresceri, 2005). The electrodes were blotted dry, immersed in solution and the pH read.

3.5.2 Determination of temperature

Effluent temperature was determined at the sampling site using a 100 ^{o}C mercury thermometer by placing the probe directly in the water.

3.5.3 Determination of Dissolved Oxygen (DO)

Dissolved oxygen was measured using a DO meter model WTW Oxi330 Oximeter DO. The probes were thoroughly rinsed with distilled deionized water before and after each reading. During each measurement, the probe was immersed approximately 30-35 mm into the sample and reading taken after stabilization.

3.5.4 Determination of Biochemical Oxygen Demand (BOD)

Biological oxygen demand was determined using BOD Oxi Top model meter as described by Yuan *et al*. (2001) after placing 50 ml and 100 ml aliquots of the sample into BOD bottles equipped with magnetic stirrer. Sodium hydroxide was then added and the bottles were tightly corked after which they were then incubated at 20 °C for 5 days. The BOD_5 values were obtained directly from the meter reading.

3.5.5 Determination of Total Suspended Solids (TSS)

To determine the suspended solids, one litre each of the original samples was filtered through a pre-weighed 1.5µm glass microfiber 47mm diameter filter paper. The filter paper was then placed on a watch glass and dried in the oven at 105 ^{o}C overnight. The filter paper containing the dried sample was then weighed and the resultant difference in weight used to calculate the TSS.

3.5.6 Determination of Total Dissolved Solids (TDS)

The filtrate obtained in 3.5.5 was placed in a dish and dried in an oven at 180 ºC.

3.5.7 Determination of Chemical Oxygen Demand (COD)

Duplicate samples were prepared for COD test as described by Fitzmaurice and Gray (1987). The reagent solutions were prepared by dissolving potassium dichromate and mercuric sulfate in 500 ml of water. Then, 1ml sulfuric acid was added and the solution diluted to 1liter. Using a pipette, 25 ml of this solution was put in a digestion tube and the contents mixed well. The tube was then subjected to gentle swirling without inversion whereby the reagents underwent rapid temperature increase. The tubes were placed in an oven at 150 ºC for 120 minutes, cooled to room temperature and then the contents were transferred to 100 ml conical flask. The volume was made to 25 ml with distilled water and then set for titration.

Titrations were done using phenolphthalein indicator which was added to the contents in the conical flask and thoroughly mixed. Titration was done until the faint blue color changed to red. The values of sample and the blank (B) titres were noted.

3.5.8 Determination of turbidity

Turbidity was measured *in situ* using turbidity meter model 2100P from HACH. The probes were thoroughly rinsed before being lowered into each solution. The reading was taken after stabilization of the system.

3.5.9 Wastewater sedimentation

From the etching tank and anodizing tank rinse water outflows, 500 ml samples were drawn and thoroughly mixed in a 1 litre measuring cylinder after adjusting the pH using 0.1M HCl or 0.1M NaOH to attain pH values of 3, 5, 7, 8 and 11. This was to find the best settling pH for getting maximum sediments. Then the mixture was allowed to settle by gravity for 24 hours and percentage settled sludge was found.

3.6 Sludge characterization

3.6.1 Determination of water content of the sludge.

Some sludge (about 40 g) was weighed in a dry porcelain dish which was then placed in an oven at 105 ^{o}C for 24 hours. The dish and its contents were cooled in a desiccator for 72 hours before weighing to obtain the sludge water content.

3.6.2 Determination of sludge non-volatile solids (ash)

The dried sludge from 3.6.1 above was further heated at 500 ^{o}C to constant weight (Patel, 2008). The difference in weight of the porcelain dish and its contents before and after drying at 500 ^{o}C was taken as the weight of the non-volatile solids.

3.7 Alum from ashed sludge cakes

Aluminium extraction from ashed sludge A, B, C, D and E (Section 3.6.2) was carried out using a 2 litre beaker which was wrapped in aluminium foil and covered with a watch glass cover. The ashed sludge was put in the beaker and the beaker placed on a laboratory hot plate. The hot plate was used to maintain temperature between 50 ^oC and 90 ^oC. To each sample, 50 ml of 2 M sulphuric acid was added. This amount was in excess of the stoichiometric ratio 1 mole Al to 1.5 moles acid i.e. 1g aluminium per 5.44 g acid. The acid was slowly added to the beaker over several minutes because rapid acid addition could result in the production of foam (Yoshikazu *et al.*, 1975). A stirring glass rod was used to mix the contents continuously. The beaker was covered during the mixing.

To the solution prepared, a calculated amount of potassium sulphate was added according to equation 1.2 in Section 1.1. whereby 1 g of Al required 3.2 g of potassium sulphate. The details of amount added are shown in Table 3.3. The solution was warmed and stirred at 30 °C for 15 minutes to dissolve the white gelatinous precipitate formed during potassium sulphate addition. The contents of the beaker were allowed to cool and then filtered to remove any undissolved material.

The filtrate was crystallized in a freezer and the crystals formed were separated from mother liquor by filtration through a piece of clean filter paper. They were washed with ethanol and dried at 30 °C in an oven for 1 hour. The dried sludge alum crystals were weighed and stored in a clean glass bottle.

Table 3.2: Preparation of alum from sludges

Sludge	A	B	C	D	E
Amount of ashed Sludge (g)	21.421	22.421	21.507	22.270	24.310
2M H_2SO_4 added (ml)	50	50	50	50	50
K_2SO_4 added (g)	23.715	24.822	23.808	24.656	26.915

Percentage yield of the product was calculated as follows:

% yield = 100(Mass of alum obtained (g) / Theoretical mass of alum expected).

3.8 Performance testing of sludge alum

3.8.1 Determination of solubility of sludge alum

An experiment was designed to find the solubility of alum product. To a clean dry boiling tube, 4 g of sludge alum was placed and then 15 ml of water was added. The mixture was warmed until the solid dissolved. A thermometer was immersed in the solution which was then cooled to the temperature at which crystals appeared. Water was added in increments of 5 ml up to 40 ml of water each time cooling to effect crystallization.

3.8.2 Coagulation of effluent and synthetic wastewater using sludge alum sludge

The effectiveness of the sludge alum recovered as described in section 3.7 above was evaluated by use of coagulation tests in jar testing apparatus. The coagulants used were raw sludge, alum made from anodizing waste and commercial alum. The raw sludge used was dried at room temperature for several days until constant weight was attained. After stabilization, the dried sludge was ground to a homogeneous powder.

The coagulation trials were done using a kaolin suspension (here referred to as synthetic wastewater) and waste effluent. The synthetic wastewater was prepared by dissolving 100 g of kaolin in 1 liter of water. The mixture was then stirred slowly at 20rpm using a flocculator SW6 for two hours resulting in a uniform suspension. This was used as stock solution in evaluation of the coagulation effectiveness of prepared alum in comparison with raw anodizing sludge and commercial alum.

The jar test apparatus was from KEWI Laboratories a Flocculator sw6 from Stuart which consisted of six jars for putting wastewater. To each jar a 0.6 mg/l dose of synthetic alum coagulant was added followed by rapid mixing, slow mixing and then allowing the mixture to settle. Turbidities of both wastewater and treated water were measured.

3.8.3 Performance of sludge alum as a coagulant

The procedure to test the effectiveness of sludge alum as a coagulant was performed using the jar test apparatus at pH 7.0 which had been established as optimum for coagulation with alum (Patel, 2008). After adding 200 ml of each wastewater to the jar, 0.6mg/l prepared alum was added. The mixture was initially stirred slowly at 30 rpm for 30 minutes and then rapidly at 80 rpm for 30minutes. The contents were then allowed to settle for one hour. This procedure was repeated using 0.6 mg/l of commercial alum. The time for the sediments to settle was taken and turbidity of the treated water was used to evaluate the effectiveness of the coagulants.

3.8.4 Optimization of coagulant dose

Similar jar tests were carried out to study the effect of coagulant dose. Nine conical flasks were each filled with 1 liter of industrial wastewater and various amounts of alum ranging from 1g to 9 g were added and mixture left to stand for 20 minutes which was the predetermined time for settlement. The final turbidity of each sample was used as an indicative parameter to verify the efficiency of coagulation and flocculation process.

3.8.5 Optimization of temperature on flocculation

An experiment was carried out to study the effect of temperature on turbidity removal. The temperature of wastewater was varied between 10 ^{o}C and 50 ^{o}C and 1.0 mg/l of sludge alum added. Turbidity of the mixture was determined as described in Section 3.5.8.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Wastewater characterization

The results obtained for various parameters of wastewater analysis are shown in Table 4.1 below.

Table 4.1: Physico-chemical characteristics of different effluent samples

Sampling Site	Temp °C	COD mg/l	pH	TSS mg/l	TDS mg/l	Turbidity NTU	DO mg/l	BOD mg/l
Feed rinse A	24.4 ±0.6	64.0 ±5.2	7.1 ±0.2	54.1 ±10.6	311.0 ± 0.10	1.77 ± 0.3	0.26 ±0.01	18.3 ±7.69
Anodizing rinse B	26.8 ±0.55	53.3 ±3.1	12.7 ±0.3	283.9 ± 70.2	696.5 ±0.12	14.94 ± 1.1	0.24 0±0.05	85.5 ±13.6
Etching rinse C	25.6 ±0.42	271.3 ±68	4.1 ±0.4	192.8 ±17.8	835.7 ±0.14	18.94 ±1.2	0.156 ±0.04	247.1 ± 29.8
Entrance to T. plant D	27.7 ±0.4	206.6 ±20.3	5.5 ±0.2	164.7 ±12.3	6777.1 ±0.31	3.29 ± 0.5	0.323 ± 0.01	132.0 ±16.4
Treatment E	28.2 ±5.8	228.0 ±1.7	5.8 ± 0.4	690.6 ±184	4619.8 ± 0.2	20.11 ± 1.5	0.251 ± 0.1	286.2 ±7.2

4.1.1. Temperature

The discharged rinse water was warmer than the feed water. The rise in temperature is attributed to the high etching temperature and the exothermic anodizing reaction. Discharges from steam generation and cooling operations also contributed to the relatively higher temperature of the final effluent mixture (27.7^{o}C± 0.4). High water temperatures result in increased solubility and thus toxicity of certain compounds especially ammonia and heavy metals such as cadmium, zinc and lead (Krenkel, 2012). The other negative effect of thermal pollution is that of increased organisms' tolerance limit which occurs because tissue permeability, metabolic rate and oxygen consumption increase with rise in water temperature.

The temperatures of all the effluents in this study were within permissible limits set by the National Environmental Management Authority Kenya, which is 20 to 35$^{\mathbf{o}}$**C** (Kaluli *et al*., 2011).

4.1.2 pH

The pH of anodizing rinse effluent was acidic (4.1) while that of the etching rinse effluent was alkaline (12.7). These values were outside the permissible limits of 6.0 to 9.0 set by Kenya Bureau of Standards (Kenya Bureau of Standards, 2016). Very high and very low pH of water discharged to a water body adversely affects aquatic life. A certain measure of neutralization to pH 5.5 was obtained when the two streams were mixed but more neutralization was required before the mixed effluent was released to the sewer.

Various industrial processes such as the one involved in this study are operated at pH values that are far from neutral. After use, the effluent is discharged, either directly into a body of water or through the local sewage treatment plant thereby contributing to the pH of the receiving body water. High or low pH is indicative of industrial pollution. Most metals become more soluble in water as the pH decreases and will negatively affect the health of aquatic organisms and also poison humans when such waters are used for drinking.

4.1.3 Total Suspended Solids (TSS)

The TSS in the various industrial effluents ranged from 53mg/l to 690.6mg/l. The set National Environmental Quality standard (NEQS) for the TSS of industrial effluents is less than 150mg/l (*et al*., 2006). The results show that the TSS of the wastewater was above permissible limits. The highest TSS could have been attributed to the rinse water effluent from the etching process which carries away the etched particles into the mixed effluent. Discharge of high levels of suspended solids into the sludge treatment facility creates an overload in the treatment plant and consequently efficiency of the treatment function. This may cause problems if directly discharged into rivers since it will be hazardous to aquatic life. Number of disease causing microbes and parasites are correlated to high level of turbidity and total suspended solids (Ho *et al*., 2003).

4.1.4 Total Dissolved Solids (TDS)

TDS values ranged between 311.0 to 6,777.1 mg/l. These values were too high and were above WHO standards permissible limits of less than 1500mg/l (Kurniawan *et al*., 2006). Total dissolved solids refer to all ion particles in solution that are smaller than two microns (Powlowicz, 2015). Elevated TDS is associated with salinity problems if discharged into irrigation water. The TDS level of a drinking water supply should be less than 500mg/l according to EPA standards (Krenkel, 2012).

Elevated levels of TDS from dissolved ions is not usually considered dangerous or harmful, and at worst results in water being “hard” (hard to make soap suds), or gives it a slightly bitter or salty taste. However, some ions such as iron and zinc dissolved in water at moderate concentrations may have beneficial health impacts (Saccone, 2017).

4.1.5 Dissolved Oxygen (DO)

This is the amount of oxygen that is dissolved in water. Results of dissolved oxygen (Table 4.1) show that the mean ranged from 0.251 to 0.323 mg/l. Dissolved oxygen is absolutely essential for the survival of aquatic organisms. For example, concentration of dissolved oxygen between 2.5 mg/l and 3 mg/l is detrimental to the life of fish. Adequate dissolved oxygen is necessary for good water quality. Oxygen affects a vast number of other water indicators, not only biochemical but also aesthetic ones like the odors, clarity and taste. Consequently, oxygen is perhaps the most well-established indicator of water quality. Dissolved oxygen levels in a water body are determined by temperatures and microbial life.

4.1.6 Biochemical Oxygen Demand (BOD)

BOD in effluents ranged between 26.0 mg/l and 316 mg/l (Table 4.1) and it was deemed to be high. The wastewater was therefore classified as heavily polluted. Increased BOD may suggest increased organic matter from industrial discharge, wastewater and effluents. Very high BOD can affect aquatic life due to depleted oxygen levels in water leading to anoxia (Akan *et al.,* 2007 and Akan *et al.,* 2008). Efficiency of any treatment plant can be judged by considering influent and effluent BOD and also the organic loading on the unit (Cresceri, 2005).

4.1.7 Chemical Oxygen Demand (COD)

The COD levels in the effluents ranged from 53.3 mg/l to 271.3 mg/l. These values were in variance with the NEMA recommended limit of 50mg/l for discharge into the surface waters. Therefore, the effluent should be treated before discharge; otherwise it may predispose aquatic environment risk (Zhou, 2008).

4.1.8 Turbidity

The mean turbidity levels ranged from 1.77mg/l to 20.11mg/l. Three sampling sites B, C and E recorded values of 14.94mg/l, 18.94mg/l and 20.11mg/l respectively. These turbidity values were slightly elevated but were within the normal ranges. Turbidity can provide food and shelter for pathogens. If not removed, turbidity can promote growth of pathogens in the distribution system leading to waterborne disease outbreaks. High turbidity levels are linked with a high number of pathogenic microbes which `cause diseases such as diarrhea, vomiting and abdominal cramp. High turbidity in water also interferes with chlorine disinfection process and provides a growth medium to pathogenic microbes (Moodley, 2007). The WHO (2006) and USEPA (2012) specifications for turbidity for drinking water is less than 5 Nephelometric Turbidity Units (ntu). To reach low levels of turbidity during water treatment, it is necessary to remove particles or suspended particulates by filtration, screening or flocculation.

4.1.9 Sedimentation of effluents.

The anodizing rinses had pH values that ranged from 3.0 to 3.6 while the pH of the etching rinses was from 9.1 to 11. When sedimentation was carried out within this pH range, the percentage settled sludge volume was as shown in Table 4.2 and Figure 4.1.

Table 4.2: Sludge Settlement at different pH Values

Solution	Nature of Solution	pH	Settled Sludge (%)
A	Strongly acidic	3	91
B	Weakly acidic	5	72
C	Neutral	7	34
D	Weakly alkaline	8	68
E	Strongly alkaline	11	82

Fig. 4.1 Effect of pH on sludge settling

The effluent settled with a clear boundary between the fluid and the solid. The pH 7.0 was found to give the iso-electric point. Aluminium hydroxide sludge acquires either a positive or negative charge and this retards compaction in sludge due to charge repulsion of opposite charges. The pH 7.0 was therefore set as a condition in subsequent settling experiments.

The solubility of dissolved aluminum in the treated water is regulated primarily by the ambient pH level. Minimum solubility for dissolved aluminum occurs in the pH range of 5.5-7.5. As long as the pH of the treated water is maintained within the range of 5.5-7.5, dissolved aluminum concentrations will be minimal.

4.2 Characterization of sludge

The five types of sludge sampled from company premises were characterized for moisture, solids and the metal ions. They were labeled A, B, C, D and E as indicated in Table 4.3.

4.2.1 Moisture content in the Sludge.

After heating the sludge for 72 hours at 105 °C, its moisture content was determined from the weight loss is shown in Table 4.3.

Table 4.3: Sludge moisture as a percentage of the initial sludge

Sludge Sample	**Initial sludge mass (g)**	**Mass after heating at 105°C for 72hrs (g)**	**Mass of Water (g)**	**% sludge moisture**
A	35.973	27.237	8.736	24.28
B	39.372	29.417	9.9553	25.26
C	32.105	25.912	5.974	18.61
D	32.791	26.942	5.8493	17.84
E	36.425	29.841	6.584	18.07

The % water contents of settled sludge of the rinse effluent mixture (Sludge A) and wastewater entering the treatment plant (Sludge B) were 24.28%, and 25.26 %, respectively. The sludge collected from the dumping site had least amount of moisture content with an average of 18.07%. The results show that the sludge produced by the anodizing process contains high water content which increases the cost of alum production.

The water in the sludge could be reduced by using some mechanical dewatering technology like the press filter which is already in use at the plant. These techniques have various advantages one of which is in the reduction of the cost of disposal through reducing the amount of bulk water in the sludge produced. The dewatered sludge can then be processed into alum. Some other mechanical methods which have been used are belt press, centrifugation technology, plate and frame filter press (Patel, 2005).

4.2.2 Volatile content of the sludge

After ashing the sludge obtained in 4.2.1 for 4 hours at 500 ^{o}C, the volatile content was determined from the weight loss and is shown in Table 4.4.

Table 4.4: Volatile content of sludge as a percentage of the initial sludge

Sludge Sample	**mass of dry sludge after heating at 105^{o}C in (g)**	**Mass after Heating 500^{o}C for 4 Hours**	**Mass of Volatile matter (g)**	**% Volatile matter of dry sludge**
A	27.237	21.421	5.816	16.17%
B	29.417	22.803	6.614	16.80%
C	25.912	21.504	4.408	13.73%
D	26.942	22.270	4.671	14.24%
E	29.841	24.310	5.531	14.60%

Non-volatile components of Sludge A which was from the mixture of effluent was found to be 16 .17% of its dry weight, while that of Sludge B obtained from the treatment plant was 16.80 % of dry weight. Sludge C obtained from the etching tank contained 13.73%, non-volatile components, while D and E sampled from two different sections of the dumping site had 14.24% and 14.60%.

4.3. Preparation of alum

Five different sludge samples described in Table 3.2 were used in alum preparation. The results obtained are presented in Table 4.5.

Table 4.5: Preparation of alum from sludge

	Sludge A	Sludge B	Sludge C	Sludge D	Sludge E
Sludge ashed at 500^oC(g)	21.421	22.803	21.504	22.270	24.310
2M H_2SO_4 Acid (ml)	50.0	50.0	50.0	50.0	50.0
K_2SO_4 used (g)	23.715	24.822	23.808	24.656	26.915
product (g)	101.68	85.244	95.210	108.178	136.021
Theoretical yield (g)	129.734	138.114	130.246	134.885	147.241
Alum recovery %	78.38	61.72	73.10	80.20	92.39
Percentage Standard deviation	+1.222	-15.438	-4.058	+3.042	+15.232

Based on Equations 1.1 and 1.2, the percentage recovery aluminium as alum for sludge A was 78.32%. The effluent sludge A had high water content and needed drying before it could be put into use, otherwise the water could cause heat production during the reaction. The aluminium content recovered was quite low compared to the other sludge samples. The amount of acid added was in excess of the required amount to ensure complete harvesting of aluminium from the sludge.

The sludge cake B collected from the treatment plant had high moisture and hence had a low percentage aluminium recovery of 61.72%. Aluminum recovery from sludge C collected from the etching tank was 73.10%. The ashes from sludge D and E sampled from two different sections of the dumping site gave the higher recoveries of 80.2% and 92.38% respectively. These two ashes were used in subsequent experiments. From the five samples used alum production was above 60% recovery which can be considered adequate.

4.4 Quality and performance of alum made from the sludge

4.4.1 Solubility of the Alum

The data for the solubility of sludge and commercial alum is given in Table D-1 in Appendix D and shown in Figure 4.2. The solubility increased with increase in temperature.

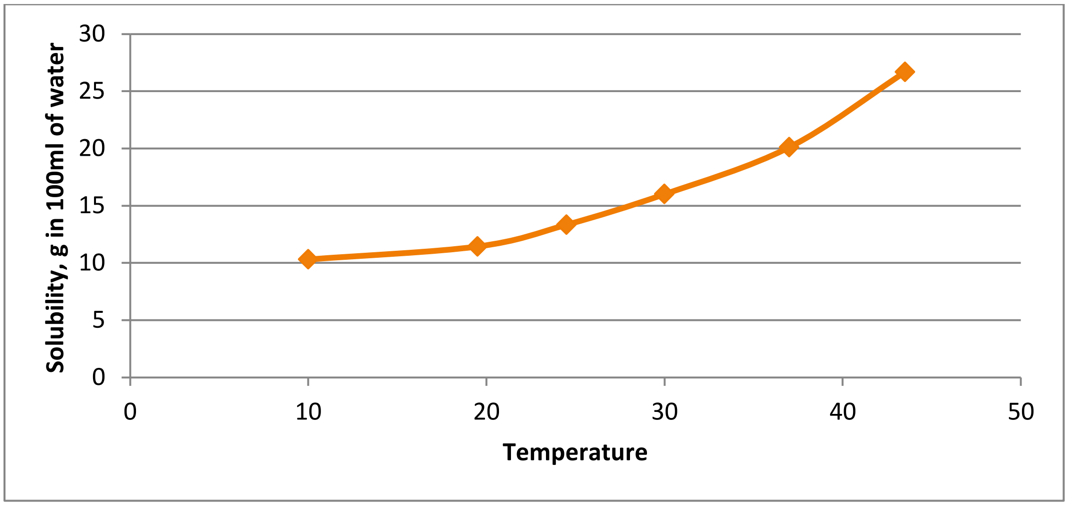

Figure 4.2 Solubility of prepared sludge alum in water

4.4.2 Coagulant dose

Results for the effect of alum dose on coagulation are presented in Figure 4.3.

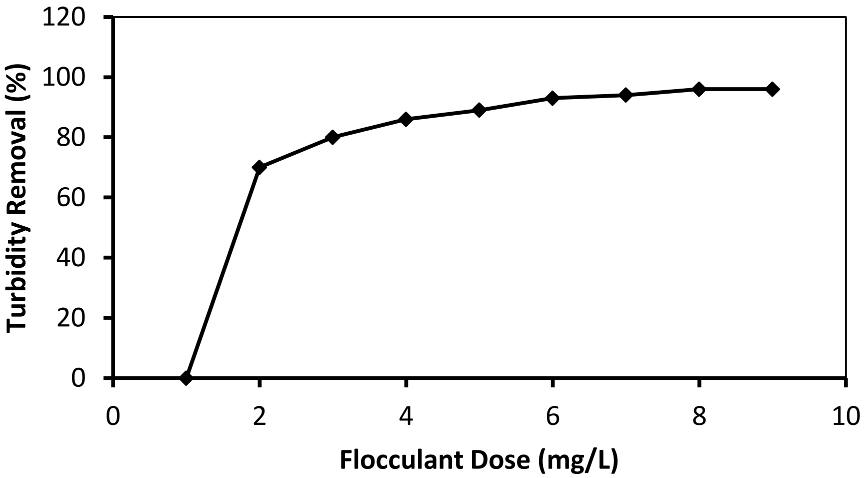

Figure 4.3 Turbidity Removal with Flocculants Dose

Turbidity removal increased quite rapidly with increase in flocculants dose and was in the range of 70 % to 86 % (Figure 4.3). At 4 mg/l alum, 80 % removal was achieved.

4.4.3 The effect of alum addition on sedimentation rate.

After addition of 0.6 mg/l of the commercial alum and 0.6 mg/l prepared sludge alum at a pH 7.0, the mixture was allowed to settle. The results are shown in Table D-2. The minimum volume of settled sludge was 29.1 % for commercial alum and 34.3% for sludge alum after 11 minutes as shown in Figure 4.4. Further sludge volume reduction occurred on settling the system for a longer time of one hour.

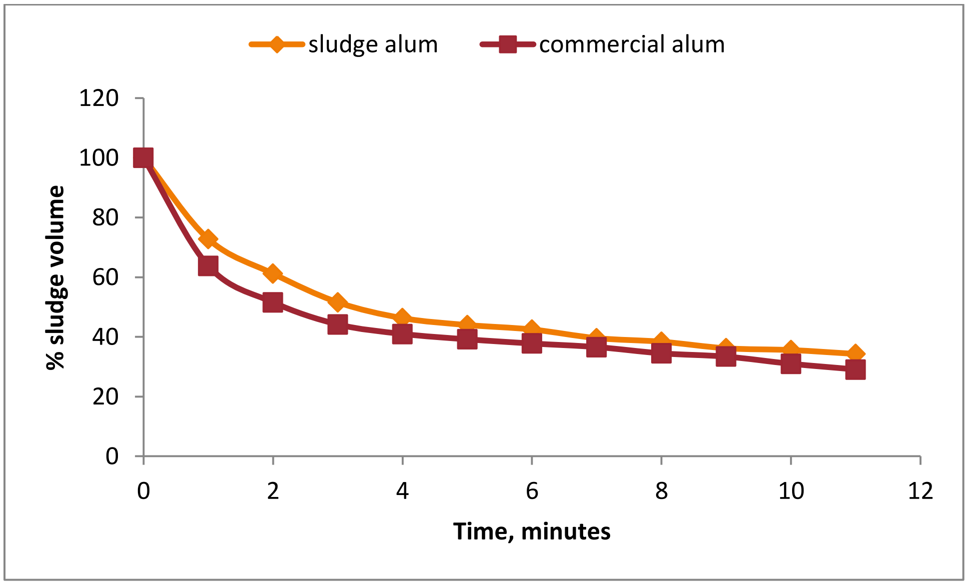

Figure 4.4 Settled sludge volume after addition of 0.6mg/l commercial alum and sludge alum

4.4.4 Pollution removal using sludge slum

Sludge alum was used to treat both industrial wastewater and synthetic effluent. Results of the main physical chemical characteristics of the two effluents before and after treatment using 0.6 mg/l sludge alum are shown in Figures 4.5 to 4.8. It is quite clear that the prepared alum was effective in reduction of total suspended and dissolved solids, turbidity, BOD and COD. The data values are shown in Table D-3 in Appendix D.

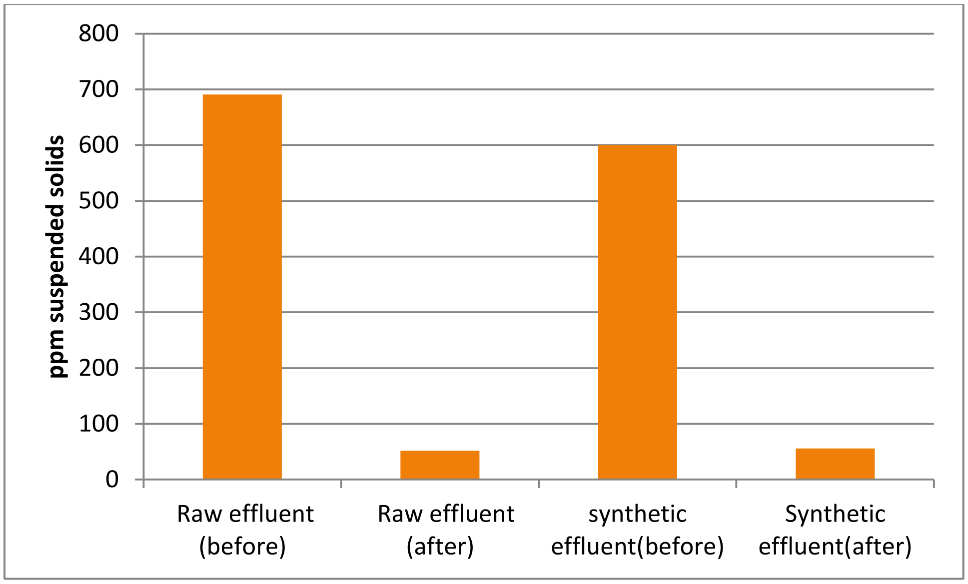

Figure 4.5 Removal of suspended solids in raw and synthetic effluent

In a colloidal suspension, particles will settle very slowly or not at all because the colloidal particles carry surface electrical charges that mutually repel each other. The purpose of a coagulant is to overcome the repulsive charge and "destabilize" the suspension. Removal of suspended solids and microorganisms occurs primarily by enmeshment and adsorption onto aluminum hydroxide precipitate according to the following net reaction:

$$Al^{+3} + 6H_2O \rightarrow Al(OH)_{3(s)} + 3H_3O^{+}$$

4.1

The aluminum hydroxide precipitate, $Al(OH)_3$, is a gelatinous floc which attracts and adsorbs colloidal particles onto the growing floc, thus reducing TSS, turbidity and pollution in general as is observed in Figures 4.5 to 4.8.

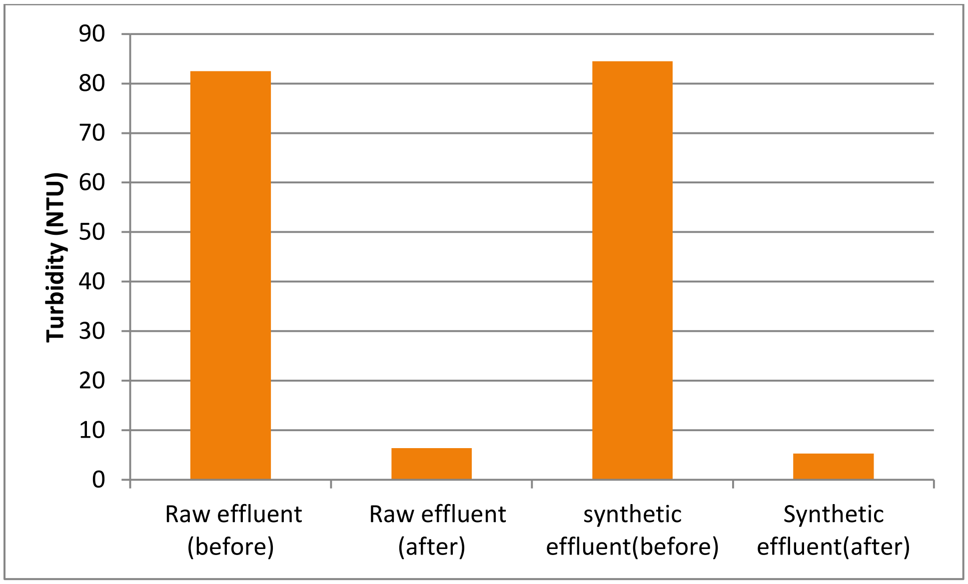

Figure 4.6 Removal of turbidity in raw and synthetic effluent

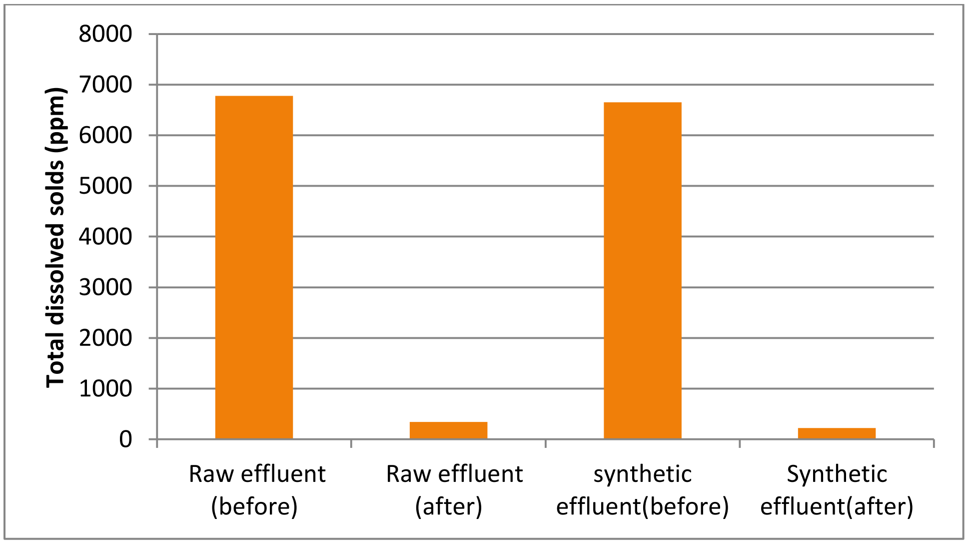

Figure 4.7 Removal of dissolved solids in raw and synthetic effluent

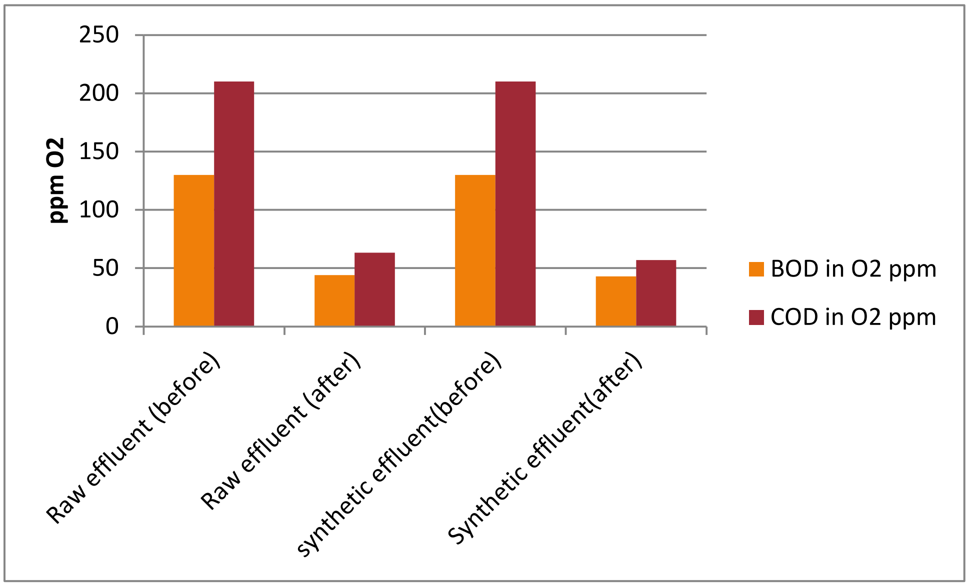

Figure 4.8 Removal of BOD and COD from raw and synthetic effluents.

The process of water treatment using alum occurs by coagulation and flocculation. These processes are investigated using the jar test, whereby coagulation and floc formation is stimulated. Wastewater under test had high BOD_5 and COD of 130 mg/L and 210 mg/L respectively and the content of suspended solid matter was 690.6 mg/l. Addition of 0.6 mg/l of alum decreased the values of the three parameters as indicated in Figures 4.6 to 4.9 and Table D-3 in Appendix D. The flocs formed were quite visible and settled rapidly and therefore coagulation process was effective. The wastewater used in the flocculation experiment had high turbidity of 82.5 NTU for industrial effluent and 84.5 NTU for the synthetic effluent. This was also decreased to 6.4 NTU and 5.3 NTU respectively making a turbidity reduction greater than 80 %. Total dissolved solids in the two effluents were very high at 6,777.1 ppm for industrial effluent and 6,650.2 ppm for synthetic effluents. After addition of 0.6 g sludge alum they were reduced to 345.2 ppm and 223.2 ppm, respectively. Similar observation was made by Mbaeze *et al*. (2017) and Abdel-Kadel *et al* (2013).

Table 4.6: Pollution removal efficiency using sludge-based alum

Parameter	% Removal efficiency in plant effluent	% Removal efficiency in synthetic effluent
Turbidity (NTU)	92.2	93.7
Susp.solid (ppm)	92.5	90.7
TDS (ppm)	94.9	96.6
BOD (ppm)	73.5	72.4
COD (ppm)	74.4	75

Removal efficiency was consistent in the two effluents and was better for turbidity, suspended solids and total dissolved solids than for BOD and COD.

4.4.5 Effect of temperature on turbidity removal

Industrial wastewaters are generated and discharged at various temperatures. The effect of temperature on the wastewater coagulation performance is given in Table D-4 in Appendices and shown in Figure 4.8.

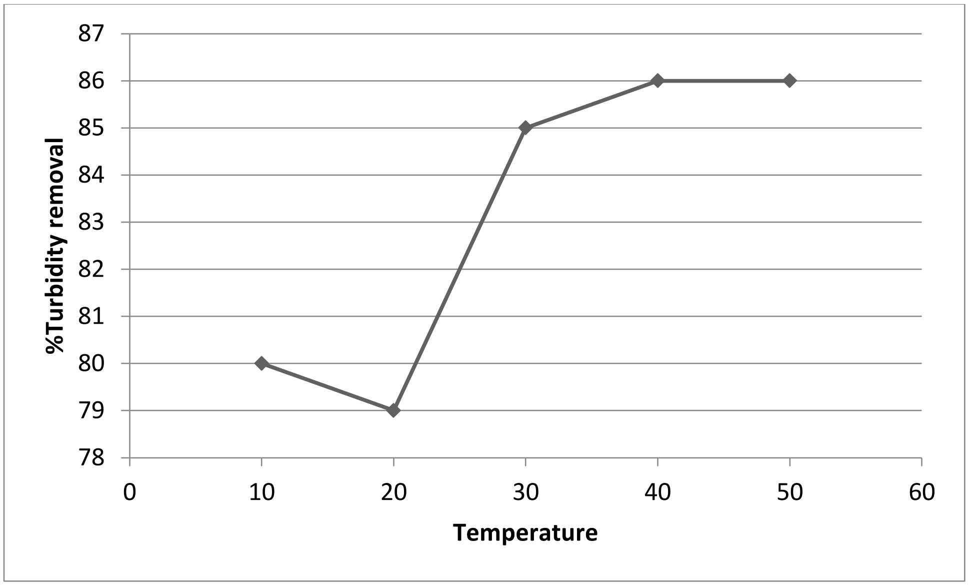

Figure 4.9: Influence of Temperature on Turbidity Removal

As the temperature was increased from 10 ^oC to 50 ^oC, turbidity removal increased from 80 % to 86 %. This is attributed to decrease in viscosity and density of the water which in turn leads to improved settling of the flocs. Therefore, alum made from the sludge would be quite effective for coagulating hot industrial effluents.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study where anodizing effluents were characterized and their potential as a source of alum was investigated. The temperature values in all the effluents were within the NEQS and WHO permissible limits. The pH of various effluents ranged from 4.1 to 12.73. Comparing with NEQS standards, the pH values of effluents were beyond permissible limits and could adversely affect aquatic life.

The TSS and TDS of the wastewater effluents sampled from various points in the anodizing plant were above the NEQS permissible limits. When wastewater with such high TSS and TDS values is directly discharged into a river or stream it will lower the aesthetic value of the water body and also affect aquatic life due to toxicity and oxygen depletion. High TSS was anticipated to cause salinity problems if discharged to waters used for irrigation downstream. The BOD levels were high compared to standards for industrial wastewater in Kenya. The anodizing plant effluent could therefore be classified as highly polluted.

The sludge produced by the anodizing plant was found to contain high amounts of water. The company could decrease the cost of disposal by reducing the amount of water. This reduction was done by settling the sludge at an optimized time followed by decantation. The amount of aluminium in the dried sludge was anticipated to be very high compared to other elements. Its recovery from the sludge and use as alum raw material was investigated. Preparation of alum and its crystallization was carried out and its performance in wastewater treatment was tested and compared to that of dried sludge and commercial alum. Alum prepared from the industrial sludge was found to be effective in coagulation and flocculation of plant and synthetic wastewater and its performance compared well with that of commercial alum. Coagulation was better at elevated temperatures and therefore, the alum could be used with hot plant effluents.

5.2 Recommendations

This study recommends that:

1. The effluents leaving the treatment plant should be monitored to ensure that they meet permitted discharge levels.
2. Pilot studies be carried out to investigate the economic viability of utilizing anodizing sludge to make alum for wastewater treatment.
3. Anticipated presence of heavy metals and hardness causing ions in sludge made from anodizing sludge limits its use. Therefore, the chemical composition of the alum prepared from sludge should be analyzed to establish whether it can be purified for use in treatment of other kind of water including for drinking water.

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APPENDICES

APPENDIX A: CHARACTERIZATION OF WASTEWATER

Table A-1: Temperature of wastewater

Sampling site	Sample 1 ^{o}C	Sample 2^{o}C	Sample 3 ^{o}C	Mean^{o} C	SD ±
Feed rinse	24.6	23.7	24.8	24.37	0.6
Etching rinse	26.3	27.4	26.8	26.83	0.55
Anodizing rinse	25.1	25.9	25.7	25.57	0.42
Effluent mixture	27.6	28.3	28.7	28.20	0.58
Treatment plant	27.4	27.3	28.0	27.73	0.40

Table A-2: Chemical oxygen Demand titration results

Sample 1

Initial cm^3	Final cm^3	Titre50ml	Mg/l
50.0	43.0	7.0	70.0
50.0	45.0	5.0	50.0
50.0	15.0	35.0	350.0
50.0	19.7	19.7	197.0
50.0	27.3	22.7	227.0

Sample 2

Initial cm^3	Final cm^3	Titre 50ml	Mg/l
50.0	43.9	6.1	61.0
50.0	44.4	5.4	54.0
50.0	26.0	23.3	233.0
50.0	30.7	23.0	230.0
50.0	27.0	23.0	230.0

Sample 3

Initial cm^3	Final cm^3	Titre 50ml	Mg/l
50.0	43.9	6.1	61.0
50.0	44.4	5.6	56.0
50.0	26.9	23.1	231.0
50.0	30.7	19.3	193.0
50.0	27.3	22.7	227.0

Table A-3 Chemical Oxygen Demand (mg/L)

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	64.0	69.2	60.8	64.4	5.2
Etching rinse	53.3	56.4	56.1	55.2	3.1
Anodizing rinse	271.0	339	298	302.7	68
Effluent mixture	206.0	214.2	226.3	215.5	20.3
Treatment plant	228.0	229.9	224.3	227.4	1.7

Table A-4 pH

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	6.8	7.2	7.2	7.1	0.2
Etching rinse	13.0	12.8	12.4	12.73	0.3
Anodizing rinse	3.9	4.6	3.8	4.1	0.4
Effluent mixture	5.3	5.4	5.7	5.47	0.2
Treatment plant	5.4	6.2	5.9	5.8	0.4

Table A-5 Total Suspended Solids

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	62.0	58.3	42.1	54.1	10.6
Etching rinse	208.2	296.7	346.8	283.8	70.2
Anodizing rinse	175.0	192.8	210.6	192.8	17.8
Effluent mixture	151.1	168.2	174.9	164.7	12.3
Treatment plant	686.7	876.2	508.9	690.6	184

Table A-6 Total Dissolved Solids

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	311.0	311.1	310.2	311.0	0.10
Etching rinse	696.7	696.3	696.6	696.5	0.12
Anodizing rinse	833.6	835.8	837.8	835.7	0.14
Effluent mixture	6781.2	6772.1	6778.0	6777.1	0.31
Treatment plant	4620.03	4620.01	4619.36	4619.8	0.23

Table A-7 Turbidity

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	2.05	1.86	1.40	1.77	0.3
Etching rinse	13.88	14.94	16.01	14.94	1.1
Anodizing rinse	18.06	20.24	18.53	18.94	1.2
Effluent mixture	3.80	2.84	3.24	3.29	0.5
Treatment plant	21.30	18.46	20.56	20.10	1.5

Table A-8 Dissolved Oxygen

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	0.26	0.27	0.26	0.260	0.01
Etching rinse	0.29	0.26	0.27	0.241	0.05
Anodizing rinse	0.16	0.13	0.17	0.152	0.04
Effluent mixture	0.33	0.32	0.31	0.320	0.01
Treatment plant	0.25	0.26	0.24	0.251	0.10

Table A-9 Biochemical Oxygen Demand

Sampling site	Sample 1	Sample 2	Sample 3	Mean	SD ±
Feed rinse	18.69	18.34	17.87	18.30	0.69
Etching rinse	88.60	85.50	82.40	85.50	0.36
Anodizing rinse	256.9	246.9	237.3	247.1	9.80
Effluent mixture	138.4	130.1	127.6	132.0	6.40
Treatment plant	290.4	289.2	279.0	286.2	7.20

APPENDIX B: CHARACTERIZATION OF SLUDGE

Table B-1 Sludge settlement at different pH values

Solution	**Solution nature**	**pH**	**Settled Sludge (%)**
A	Strongly acidic	3	91
B	Weakly acidic	5	72
C	Neutral	7	34
D	Weakly alkaline	8	68
E	Strongly alkaline	11	82

Table B-2 Sludge moisture as a percentage of the initial sludge

Sludge Sample	Initial sludge mass (g)	Mass after heating at 105 ºC for 72 hrs (g)	Mass of Water (g)	% sludge moisture
A	35.973	27.237	8.736	24.28
B	39.372	29.417	9.9553	25.26
C	32.105	25.912	5.974	18.61
D	32.791	26.942	5.8493	17.84
E	36.425	29.841	6.584	18.07

Table B-3 Non Volatile Content of Sludge as a Percentage of the Initial Sludge

Sludge Sample	**Weight of dry sludge after in**	**Heating 500ºC 4**	**Mass of Non Volatile**	**% Non Volatile of**

	(g)	**Hours**	**Solid(g)**	**Initial Solid**
A	27.237	21.421	5.816	16.17%
B	29.417	22.803	6.614	16.80%
C	25.912	21.504	4.408	13.73%
D	26.942	22.270	4.671	14.24%
E	29.841	24.310	5.531	14.60%

APPENDIX C: PREPARATION OF ALUM

Table C-1 Preparation of alum from sludge A

	Sludge A
Total amount of sludge (g)	35.973
Heated at 100 ^{o}C (g)	27.237
Amount of moisture (g)	**8.736**
Sludge ashed at 500 ^{o}C(g)	21.421
Volatile matter (g)	**5.816**
2M H_2SO_4 Acid (ml)	50.0
K_2SO_4 used (g)	23.715
product in grams	101.68
Theoretical yield	129.734
Alum recovery %	**78.38**

Table C-2 Preparation of Alum from sludges B

	Sludge B
Total amount of sludge (g)	39.372
After heating at 100 ^{o}C (g)	29.417
Amount of moisture (g)	**9.955**
Weight after ashing at 500 ^{o}C(g)	22.803
Volatile matter (g)	**6.614**
2M H_2SO_4 Acid (ml)	50.0

K_2SO_4 used (g)	24.822
product in grams	85.244
Theoretical yield	138.114
Alum recovery %	**85.24**

Table C-3 Preparation of Alum from sludge's C

	Sludge C
Total amount of sludge (g)	32.105
Heated at 100 °C (g)	25.912
Amount of moisture (g)	**6.199**
Sludge ashed at 500 °C(g)	21.504
Volatile matter (g)	**4.408**
2M H_2SO_4 Acid (ml)	50.0
K_2SO_4 used (g)	23.808
product in grams	95.210
Theoretical yield	130.246
Alum recovery %	**73.10**

Table C-4 Preparation of Alum from sludge D

	Sludge D
Total amount of sludge (g)	32.791
Heated at 100 °C (g)	26.942

Amount of moisture (g)	**5.849**
Sludge ashed at 500 ^oC(g)	22.270
Volatile matter (g)	**4.672**
2M H_2SO_4 Acid (ml)	50.0
K_2SO_4 used (g)	24.656
product in grams	108.178
Theoretical yield	134.885
Alum recovery %	**80.20**

Table C-5 Preparation of Alum from sludge E

	Sludge E
Total amount of sludge (g)	36.425
Heated at 100 ^oC (g)	29.841
Amount of moisture (g)	**6.584**
Sludge ashed at 500 ^oC(g)	24.310
Volatile matter (g)	**5.531**
2M H_2SO_4 Acid (ml)	50.0
K_2SO_4 used (g)	26.915
product (g)	136.021
Theoretical yield	147.241
Alum recovery %	**92.39**

APPENDIX D: ALUM SOLUBILITY AND PERFORMANCE IN WASTEWATER TREATMENT

Table D-1 Solubility of sludge alum and commercial alum

Cummulative amount of water added to 4g alum cm^3	Crystallization Temp ^oC Sludge alum	Crystallization Temp ^oC Commercial alum	Amount of alum in g/100 g H_2O
15	43.5	47.2	26.67
20	37.0	38.4	20.1
25	30.0	32.3	16.0
30	24.5	28.0	13.33
35	19.5	22.4	11.43
40	10.0	19.8	10.30

Table D-2 Percent settled sludge volume after addition of 0.6mg/l sludge alum and commercial alum

Time, minutes	Sludge alum		Commercial alum	
0	Sludge Volume in a litre (ml)	% sludge volume	Sludge Volume in a litre (ml)	% sludge volume
0	1000	100	100	100
1	728	72.8	638	63.8
2	612	61.2	516	51.6

3	516	51.6	442	44.2
4	463	46.3	41o	41.0
5	440	44.0	392	39.2
6	425	42.5	378	37.8
7	396	39.6	366	36.6
8	384	38.4	345	34.5
9	362	36.2	334	33.4
10	356	35.6	310	31.0
11	343	34.3	291	29.1

Table D-3 Results of wastewater treatment using sludge alum

Parameter	Plant effluent (before)	Plant effluent (after)	% Removal	Synthetic effluent (before)	Synthetic effluent (after)	% Removal
Turbidity (NTU)	82.5	6.4	92.2	84.5	5.3	93.7
Susp.solid (ppm)	690.6	52.0	92.5	600.4	56.0	90.7
TDS (ppm)	6777.1	345.2	94.9	6650.2	223.3	96.6
BOD (ppm)	151	40	73.5	152	42	72.4
COD (ppm)	207	53	74.4	208	52	75

Table D-4 Effect of temperature on turbidity removal

Temp in ^{o}C	% Turbidity removal
10	80
20	79
30	85
40	86
50	86